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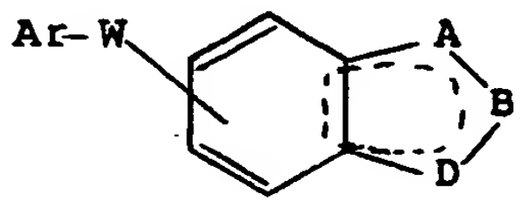
(54) **Substituted benzimidazole and indazole derivatives, processes for their preparation and their use as herbicides.**

(57) A herbicidal compound of formula (I) :



(I)

or N-oxide or quaternised derivative thereof;
in which the dotted lines indicate the presence of two double bonds arranged so as to form a fused hetero-aromatic ring system;
Ar is an optionally substituted aryl or heterocyclic ring system;
W is O or NR^1
where R^1 is H or lower alkyl;
A, B, D are independently selected from N, NR^2, N-E, CR^5, C-E or $C(R^5)E$;
wherein E is:

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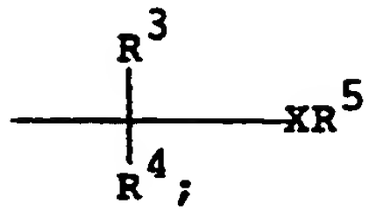


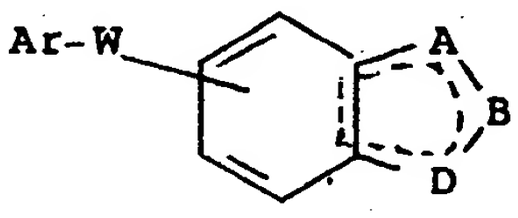
provided 2 of A, B and D are N, NR^2 or N-E and at least one of A, B or D carries a group E;
where R^2 is H, OR^7, CN, $COOR^8$, alkyl or haloalkyl;
R^3 and R^4 are independently selected from H, optionally substituted alkyl, alkenyl or alkynyl, halogen, NR^9R^{10}, or
R^3 and R^4 together with the carbon to which they are attached form an optionally substituted alkenyl or cycloalkyl group;
R^5 is CO_2R^{11}, CN, COR^{11}, CH_2OR^{11}, $CH(OH)R^{11}$, $CH(OR^{11})R^{12}$, $CSNH_2$, $COSR^{11}$, $CSOR^{11}$, $CONHSO_2R^{11}$, $CONR^{13}R^{14}$, $CONHNR^{13}R^{14}$, $CONHN^+R^{13}R^{14}R^{15}$ Y^-, $CO_2^-M^+$ or $COON=CR^{13}R^{14}$;
X is $(CH_2)_n$, CH=CH, $CH(OR^{15})CH_2$ or $COCH_2$;
where n is 0, 1 or 2;
M^+ is an agriculturally acceptable cation;
Y^- is an agriculturally acceptable anion;
R^6 is H, halogen, OR^7, CN, $COOR^8$, alkyl or haloalkyl;
R^7 and R^8 are independently H or lower alkyl;
R^{11}, R^{12} and R^{15} are independently selected from H or an optionally substituted alkyl, alkenyl, alkynyl or aryl group; and
R^9, R^{10}, R^{13}, R^{14} and R^{15} are independently selected from H or an optionally substituted alkyl, alkenyl, alkynyl or aryl group or any two of R^9, R^{10}, R^{13}, R^{14} and R^{15} together with the atom to which they are attached form a cycloalkyl or heterocyclic ring providing that the compound is other than 5-(2,4-dichlorophenoxy)indazol-1-ylacetic acid or its methyl ester.
Process for the preparation of these compounds and compositions containing them are also described.

The present invention relates to novel substituted benzimidazole and indazole derivatives, processes for their preparation, their use as herbicides and herbicidal compositions containing them.

European Patent No. 178,708 A describes certain benzheterocyclic-phenyl ether derivatives which have herbicidal activity.

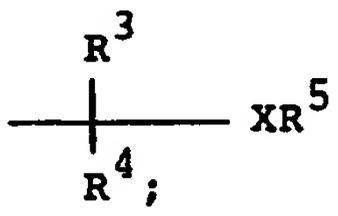
Japanese Patent Kokai No. 59-98060 describes certain indazole derivatives.

According to the present invention there is provided a compound of formula (I) :



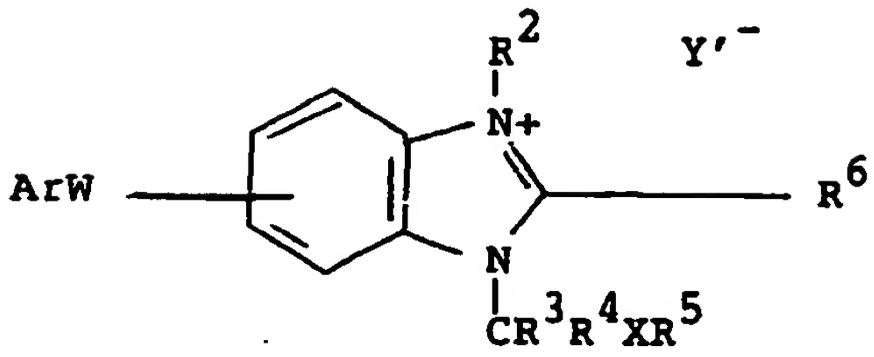
(I)

or N-oxide or quaternised derivative thereof;
in which
the dotted lines indicate the presence of two double bonds arranged so as to form a fused hetero-aromatic ring system;
Ar is an optionally substituted aryl or heterocyclic ring system;
W is 0 or NR^1
where R^1 is H or lower alkyl;
A, B, D are independently selected from N, NR^2, N-E, CR^6, C-E or $C(R^6)E$;
wherein E is:



provided 2 of A, B and D are N, NR^2 or N-E and at least one of A, B or D carries a group E;
where R^2 is H, OR^7, CN, $COOR^8$, alkyl or haloalkyl;
R^3 and R^4 are independently selected from H, optionally substituted alkyl, alkenyl or alkynyl, halogen, NR^9R^{10}, or
R^3 and R^4 together with the carbon to which they are attached form an optionally substituted alkenyl or cycloalkyl group;
R^5 is CO_2R^{11}, CN, COR^{11}, CH_2OR^{11}, $CH(OH)R^{11}$, $CH(OR^{11})R^{12}$, $CSNH_2$, $COSR^{11}$, $CSOR^{11}$, $CONHSO_2R^{11}$, $CONR^{13}R^{14}$, $CONHNR^{13}R^{14}$, $CONHN^+R^{13}R^{14}R^{15}$ Y^-, $CO_2^-M^+$ or $COON=CR^{13}R^{14}$;
x is $(CH_2)_n$, CH=CH, $CH(OR^{16})CH_2$ or $COCH_2$;
where n is O, 1 or 2;
M+ is an agriculturally acceptable cation;
Y^- is an agriculturally acceptable anion;
R^6 is H, halogen, OR^7, CN, $COOR^8$, alkyl or haloalkyl;
R^7 and R^8 are independently H or lower alkyl;
R^{11}, R^{12} and R^{16} are independently selected from H or an optionally substituted alkyl, alkenyl, alkynyl or aryl group; and
R^9 R^{10}, R^{13}, R^{14} and R^{15} are independently selected from H or an optionally substituted alkyl, alkenyl, alkynyl or aryl group or any two of R^9, R^{10}, R^{13}, R^{14} and R^{15} together with the atom to which they are attached form a cycloalkyl or heterocyclic ring providing that the compound is other than 5-(2,4-dichlorophenoxy)indazol-1-ylacetic acid or its methyl ester.

Quaternised derivatives of compounds of formula (I) are compounds obtained by reacting a compound of formula (I) with a quaternising agent such as an alkyl halide or a trialkyloxonium species. It is believed that such quaternised derivatives carry a charge on a single nitrogen atom, and this is on an NR^2 group within the molecule in preference to an N-E group. For example, where A is NR^2, B is CR^6 and D is $NCR^3R^4XR^5$, the quaternised derivative is believed to have the formula:



where Ar, W, R^2, R^3, R^4, R^5, R^6 and X are as defined in relation to formula (I) and Y'^- is an anion derived from the quaternising agent such as a halide, tetrafluoroborate, mesylate or tosylate ion.

As used herein the term "alkyl" includes straight or branched chains containing up to 10 carbon atoms preferably from 1 to 6 carbon atoms. The terms "alkenyl" and "alkynyl" refer to unsaturated straight or branched chains having from 2 to 10 and preferably from 2 to 6 carbon atoms. The term "cycloalkyl" includes rings containing from 3 to 9 carbon atoms, preferably from 3 to 6 carbon atoms. The term "alkoxy" includes straight or branched chains containing up to 10 carbon atoms preferably from 1 to 6 carbon atoms.

The term "lower" used in relation to alkyl, alkoxy, alkenyl or alkynyl groups means that the group contains up to 3 carbon atoms.

The term "haloalkyl" and "haloalkoxy" refer to alkyl and alkoxy groups respectively substituted by at least one halogen atom such as fluorine, chlorine or bromine. A particular haloalkyl group is trifluoromethyl. The term "aryl" includes phenyl and naphthyl. The term "heterocyclic" includes rings of up to 10 atoms, preferably up to 6 atoms up to 3 of which are selected from oxygen, nitrogen or sulphur. The term halogen includes fluorine, chlorine, bromine and iodine.

A suitable aryl ring system is phenyl.

Suitable heterocyclic ring systems for Ar are rings of up to 10 atoms, up to 3 of which are selected from oxygen, nitrogen or sulphur, preferably aromatic ring systems such as pyridine and pyrazole.

Suitable optional substitutents for the aryl or heterocyclic ring systems Ar and for the aryl groups R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} are up to 5 preferably up to 3 members selected from halogen (fluoro, chloro, bromo or iodo), lower alkyl, haloalkyl (for example CF_3), haloalkoxy (for example OCF_3), nitro, cyano, lower alkoxy (for example methoxy) or $S(O)_pR^a$ where p is 0, 1 or 2 and R^a is alkyl (for example thiomethyl, sulphinylmethyl and sulphonylmethyl).

Preferred positions of substitution when the aryl ring is a phenyl ring are the 2, 4 and 6 positions, particularly 2,4,6-tri- substituted rings with a trifluoromethyl group at the 4-position.

Examples of optional substituents for alkyl, alkenyl, alkynyl groups R^3, R^4, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} include one or more groups selected from halo such as fluoro, chloro or bromo; nitro; nitrile; aryl such as phenyl; CO_2R^{17}, $NHCOR^{17}$ or $NHCH_2CO_2R^{17}$ wherein R^{17} is hydrogen, C_{1-6} alkyl or an agriculturally acceptable cation; C_{1-6} alkoxy; oxo; $S(O)_pR^a$ where p is 0, 1 or 2 and R^a is alkyl (for example thiomethyl, sulphinylmethyl and sulphonylmethyl); amino; mono- or di- C_{1-6} alkylamino; $CONR^{18}R^{19}$ wherein R^{18} and and R^{19} are independently selected from hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl or C_{2-6} alkynyl or R^{18} and R^{19} are joined together to form a heterocyclic ring having up to 7 ring atoms 3 of which may be selected from oxygen, nitrogen or sulphur. An example of a heterocyclic substitutent is tetrahydrofuranyl.

Examples of agriculturally acceptable anions for Y^- are halides, tetrafluoroborate, mesylate and tosylate.

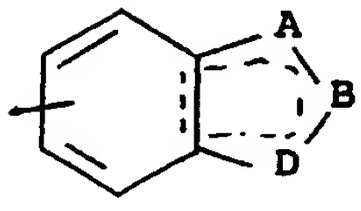
Examples of agriculturally acceptable cations for R^{17} and M^+ are sodium, potassium or calcium ions, sulphonium or sulphoxonium ions for example of formula $S^+(O)_qR^9R^{10}R^{13}$ where q is 0, or 1 and R^9, R^{10} and R^{13} are as herinbefore defined or ammonium or tertiary ammonium ions of formula $N^+R^9R^{10}R^{13}R^{14}$ where R^9, R^{10}, R^{13} and R^{14} are as herinbefore defined. Suitable substituents for the alkyl, alkenyl and alkynyl groups in these cations are hydroxy and phenyl. Suitably where any of R^9, R^{10}, R^{13} and R^{14} in these cations are optionally substituted alkyl, they contain from 1 to 4 carbon atoms.

Particular examples of R^9, R^{10}, R^{13} and R^{14} in these cations are hydrogen, ethyl, isopropyl, benzyl, and 2-hydroxyethyl.

Suitable halo groups R^3, R^6, and R^{14} include fluorine, chlorine and bromine.

Suitable heterocyclic rings formed from two of R^9, R^{10} R^{13} R^{14} and R^{15} and the atom to which they are attached are pyrrolidine, piperidine and morpholine.

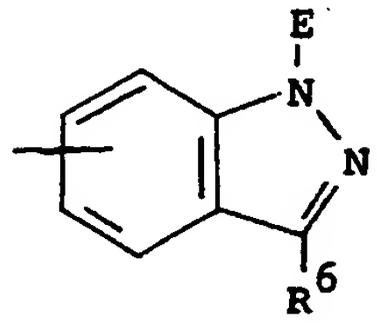
Suitable groups of sub-formula (i):



(i)

are the following groups:

(a)



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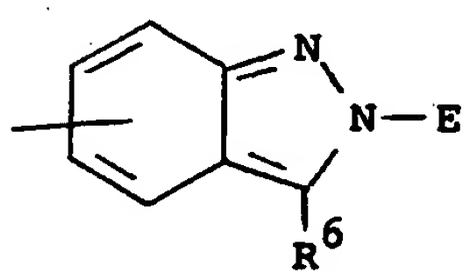
(b)



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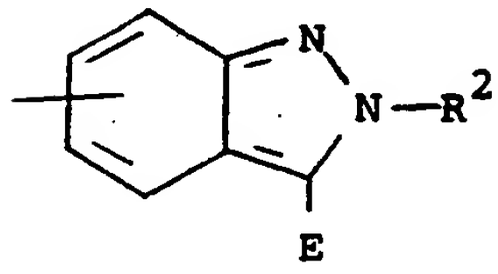
(c)



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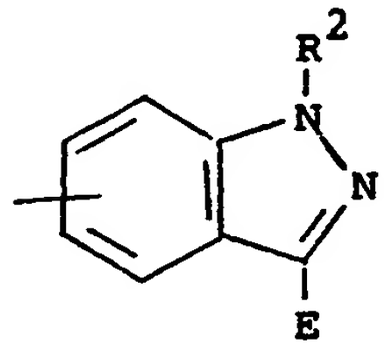
(d)



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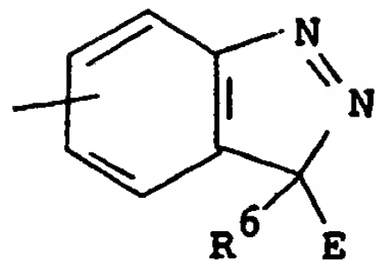
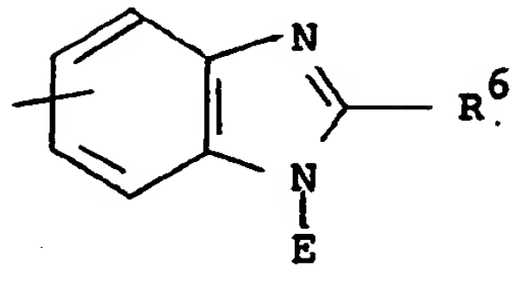
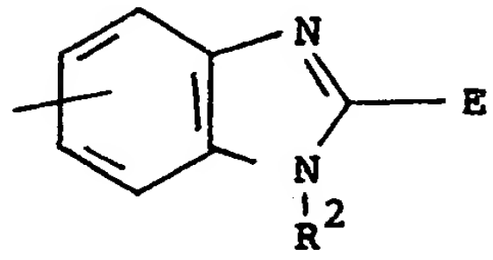
(e)  ;

(f)  or

(g) 

Preferably the group of sub-formula (i) is group (a) or (f) as defined above.

Preferably R^3 is H.

Preferably R^4 is H or is C_{1-3} alkyl, in particular methyl.

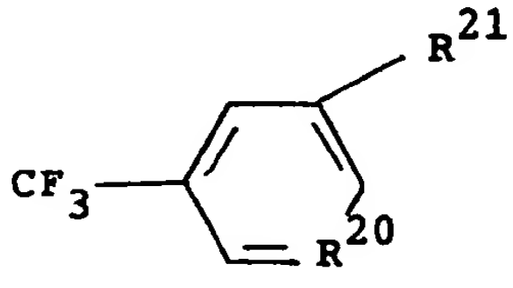
Suitably R^5 is CO_2R^{11}, $CONR^{13}R^{14}$, $CONHSO_2R^{11}$, $COON=CR^{13}R^{14}$, $CONHNR^{13}R^{14}$ or $CONHN^+R^{13}R^{14}R^{15}\ Y^-$.

Preferably R^5 is CO_2R^{11}.

R^{11} is suitably C_{1-6} alkyl or substituted alkyl such as alkoxyalkyl or oxo substituted alkyl.

Preferably R11 is methyl or ethyl.

Ar is preferably a group:



where R^{20} is N, CH or CR^{22}; R^{21} and R^{22} are independently selected from halogen such as chlorine or fluorine.

Preferably R^{20} is CR^{22} and most preferably one of R^{21} and R^{22} is chlorine and the other is fluorine.

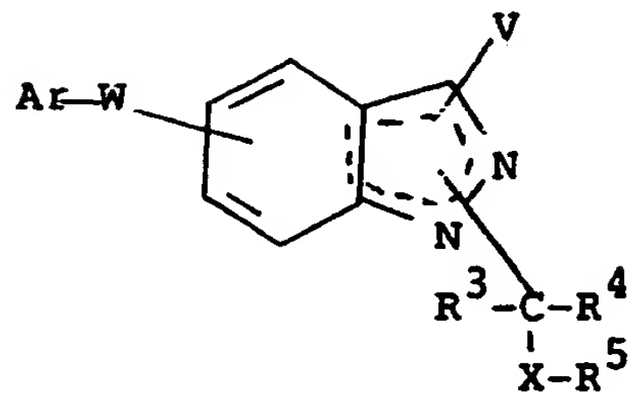
W is preferably oxygen.

Preferably X is $(CH_2)n$ where n is zero or 1, especially zero.

When the group of sub-formula (i) is group (a) above, R^6 is preferably H or Cl.

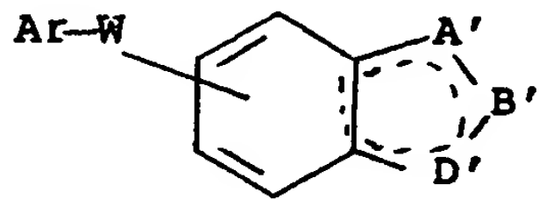
When the group of sub-formula (i) is group (f) above, R^6 is preferably H, CH_3, CF_3 or CN.

An example of a sub-group of formula (I) are compounds of formula (IA):



(IA)

in which the dotted lines indicate the presence of two double bonds arranged so as to form a fused heteroaromatic ring system;
Ar, W, X, R^3 , R^4 and R^5 are as defined in relation to formula (I) and
V is H, halogen, OR^7, CN, $COOR^8$, alkyl or haloalkyl provided that when V is halogen it is not attached to a nitrogen atom and further provided that the compound is other than 5-(2,4-dichlorophenoxy)indazol-1-ylacetic acid or its methyl ester.
A further example of a sub-group of formula (I) are compounds of formula (IC):



(IC)

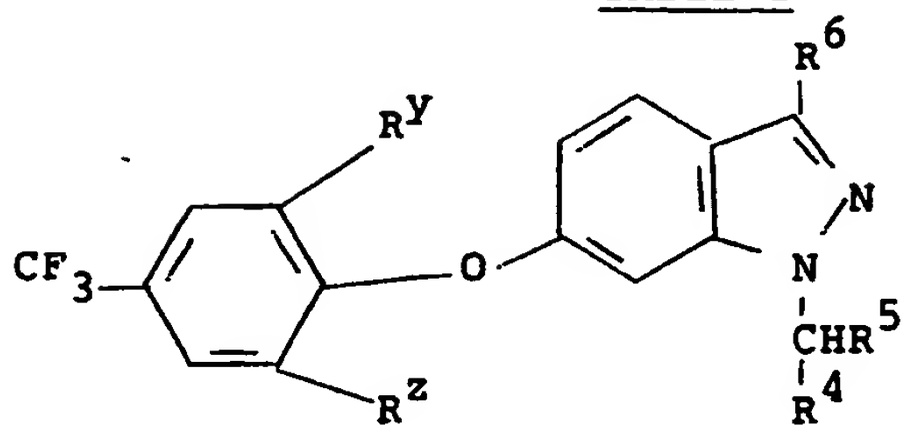
or a quaternised derivative thereof;
in which
Ar and W are as defined in relation to formula (I) and
A' is N, NH or N-lower alkyl;
B' is C-R^6 or C-E;
D' is N-E, NH or N-lower alkyl provided that when B' is C-R^6, D' is not NH or N-lower alkyl; and
E and R^6 are as defined in relation to formula (I).

The formula (I) given above is intended to include tautomeric forms of the structure drawn, as well as physically distinguishable modifications of the compounds which may arise, for example, from different ways in which the molecules are arranged in a crystal lattice, or from the inability of parts of the molecule to rotate freely in relation to other parts, or from geometrical isomerism, or from intra-molelcular or intermolecular hydrogen bonding, or otherwise.

Some of the compounds of the invention can exist in enantiomeric forms. The invention includes both individual enantiomers and mixtures of the two in all proportions.

Particular examples of compounds according to the invention are listed in Tables I,II, III, IV and V. Characterising data for the compounds are given in Table VI.

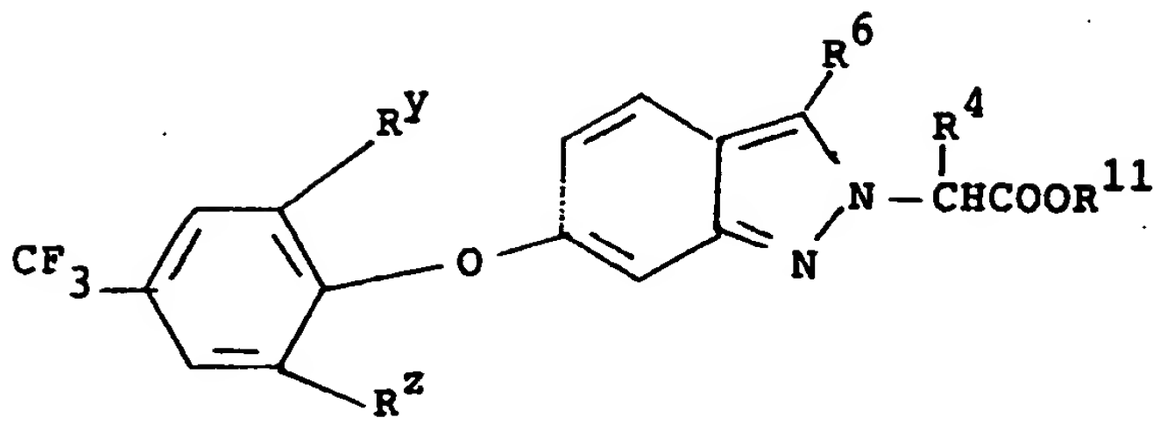
TABLE I



Compound No	R^Y	R^Z	R^4	R^5	R^6
1	F	Cl	CH_3	$CO_2C_2H_5$	H
2	F	Cl	H	$CO_2C_2H_5$	H
3	F	Cl	CH_3	CO_2H	H
4	F	Cl	H	CO_2H	H
5	F	Cl	H	CO_2CH_3	H
6	Cl	Cl	CH_3	$CO_2C_2H_5$	H
7	H	NO_2	CH_3	$CO_2C_2H_5$	H
8	H	CN	CH_3	$CO_2C_2H_5$	H
9	H	Cl	CH_3	$CO_2C_2H_5$	H
10	F	Cl	CH_3	CO_2CH_3	H
11	F	Cl	CH_3	CO_2nPr	H
12	F	Cl	CH_3	CO_2nBu	H
13	F	Cl	CH_3	$CO_2C_2H_5$	Cl
14	CN	Cl	CH_3	$CO_2C_2H_5$	H
15	NO_2	Cl	CH_3	$CO_2C_2H_5$	Cl
16	CN	Br	CH_3	$CO_2C_2H_5$	Cl
17	NO_2	NO_2	CH_3	$CO_2C_2H_5$	Cl
19	F	Cl	CH_3	$CONH_2$	Cl
20	F	Cl	CH_3	$CONHN(CH_3)_3^+I^-$	Cl
21	H	Cl	H	$CO_2C_2H_5$	Cl

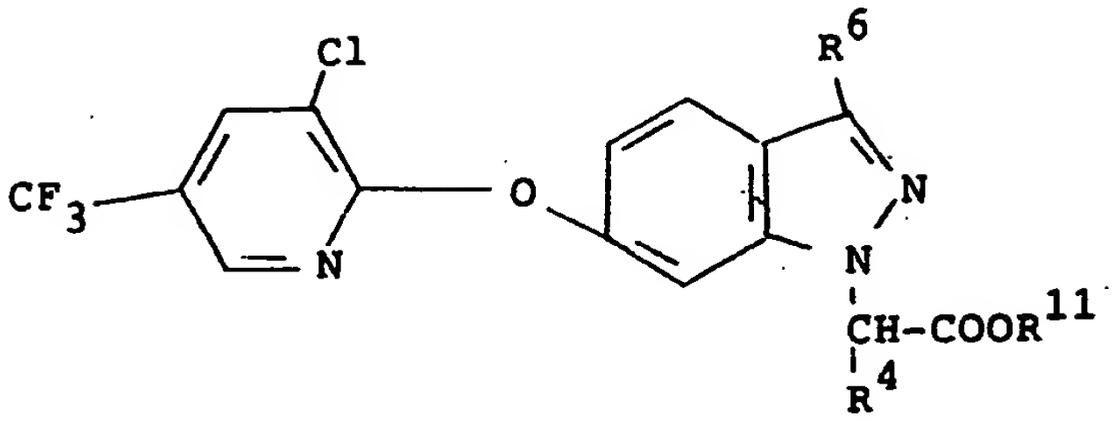
Compound No	R^Y	R^Z	R^4	R^5	R^6
22	H	NO_2	H	$CO_2C_2H_5$	Cl
23	H	CN	H	$CO_2C_2H_5$	Cl
24	H	Cl	H	$CO_2C_2H_5$	Cl
25	H	NO_2	H	$CO_2C_2H_5$	Cl
26	H	CN	H	$CO_2C_2H_5$	Cl
27	F	Cl	H	CO_2H	Cl
28	F	Cl	H	CO_2CH_3	Cl
29	F	Cl	H	CO_2nPr	Cl
30	F	Cl	H	CO_2nBu	Cl
31	F	Cl	H	$CO_2C_2H_5$	Cl
32	F	Cl	CH_3	$CONHN(CH_3)_2$	H
40	F	Cl	CH_3	CO_2H	Cl
41	F	Cl	CH_3	$CO_2^-Na^+$	H
42	F	Cl	CH_3	CO_2CH_3	Cl
43	F	Cl	CH_3	CO_2iPr	Cl
44	F	Cl	CH_3	CO_2nBu	Cl
45	F	Cl	CH_3	CO_2nPr	Cl
46	F	Cl	CH_3	$CO_2(CH_2)_2OCH_3$	Cl
47	F	Cl	CH_3	$CO_2N{=}C(CH_3)_2$	Cl
48	Cl	Cl	CH_3	$CO_2C_2H_5$	Cl
49	H	CN	CH_3	$CO_2C_2H_5$	Cl
50	Cl	CN	CH_3	$CO_2C_2H_5$	Cl
51	F	Cl	CH_3	CO_2–  –NO_2	H
52	F	Cl	CH_3	$CO_2N{=}C(CH_3)_2$	H
53	Cl	Cl	CH_3	CO_2H	Cl
54	H	CN	CH_3	CO_2H	Cl
55	Cl	CN	CH_3	CO_2H	Cl

TABLE II



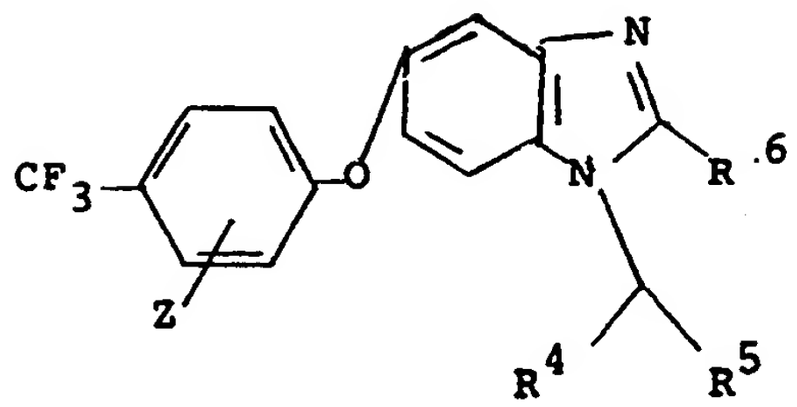
Compound No	R^Y	R^Z	R^4	R^{11}	R^6
33	F	Cl	CH_3	C_2H_5	H
34	F	Cl	H	C_2H_5	H
35	F	Cl	CH_3	CH_3	H
36	F	Cl	CH_3	H	H

TABLE III



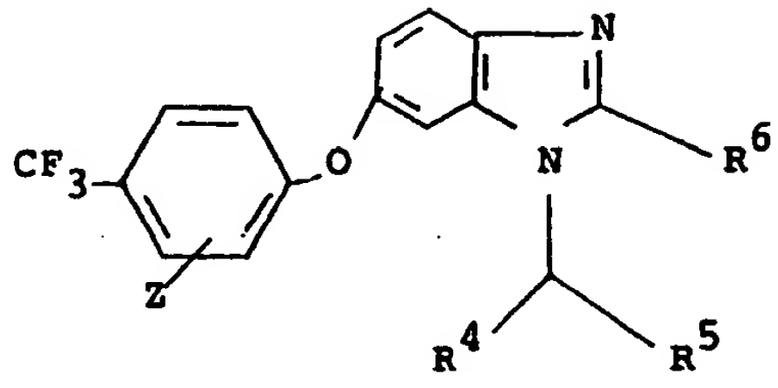
Compound No.	R^4	R^{11}	R^6
37	CH_3	C_2H_5	H
38	H	C_2H_5	H
39	H	C_2H_5	Cl

TABLE IV



COMPOUND	R^4	R^5	R^6	Z
61	CH_3	COOEt	CF_3	2-Cl,6-F
62	CH_3	COOEt	CH_3	2-Cl,6-F
63	CH_3	COOEt	CH_3	2-Cl
64	CH_3	COOEt	H	$2-NO_2$
65	CH_3	COOEt	H	2-CN
66	CH_3	COOEt	H	2-Cl
67	CH_3	COOEt	H	2-Cl,6-F
68	H	COOEt	H	2-Cl,6-F
69	H	COOEt	CF_3	2-Cl,6-F
70	H	COOEt	CF_3	2-CN
71	H	COOEt	CF_3	2-Cl
72	H	COOH	CF_3	2-Cl,6-F
73	H	$CONH_2$	CF_3	2-Cl,6-F
74	H	CONHEt	CF_3	2-Cl,6-F
100	CH_3	COOEt	CN	2-Cl,6-F
102	CH_3	COOMe	CN	2-Cl,6-F
103	CH_3	COOiPr	CN	2-Cl,6-F
104	H	COOMe	CN	2-Cl,6-F
108	H	COOEt	CF_3	$2-NO_2$

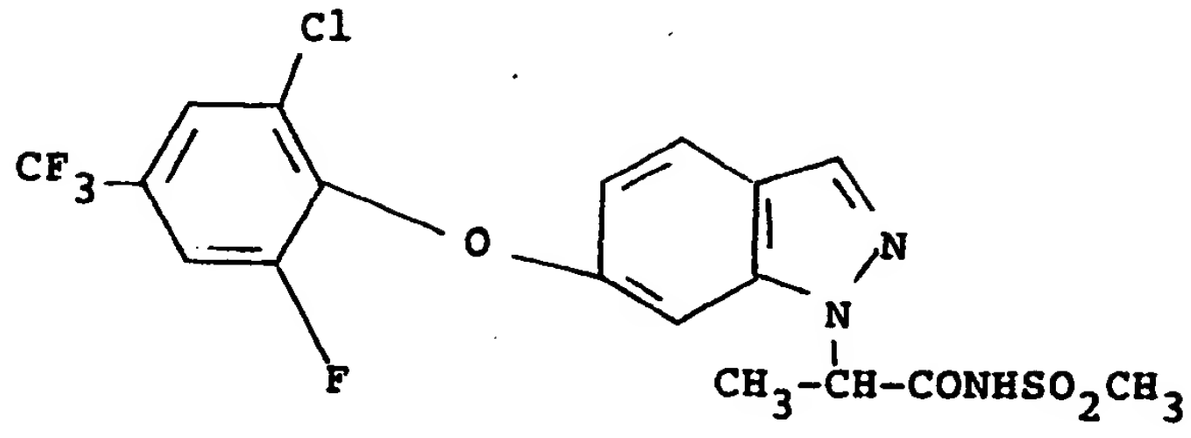
TABLE V



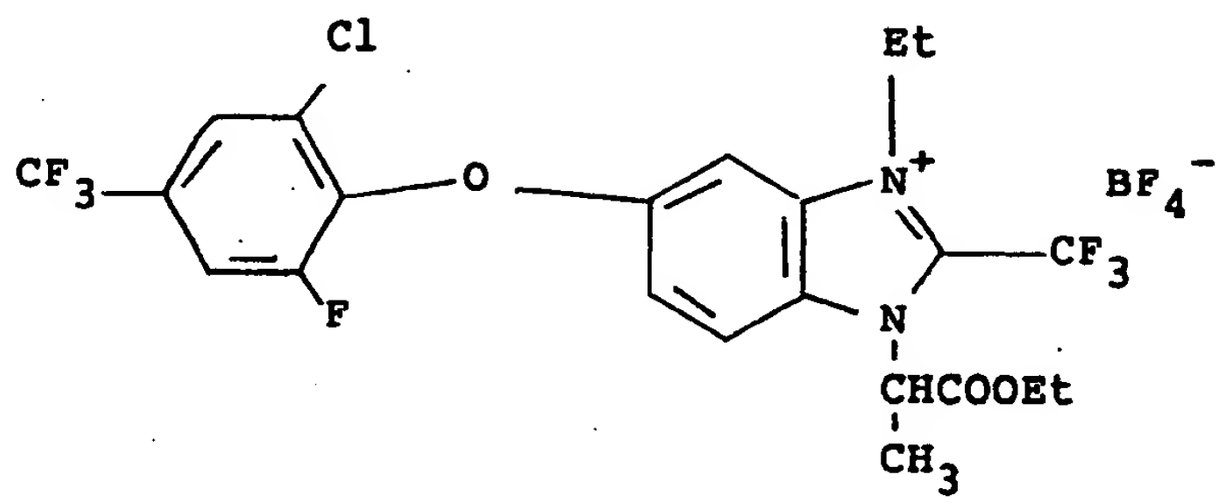
COMPOUND	R^4	R^5	R^6	Z
75	Me	COOEt	CF_3	2-Cl,6-F
76	Me	COOH	CF_3	2-Cl,6-F
77	Me	COOEt	Me	2-Cl,6-F
78	Me	COOEt	Me	2-Cl
79	Me	COOEt	H	$2-NO_2$
80	Me	COOEt	H	2-CN
81	Me	COOEt	H	2-Cl
82	Me	COOEt	H	2-Cl,6-Cl
83	H	COOEt	H	2-Cl,6-F
84	H	COOEt	CF_3	2-Cl,6-F
85	H	COOEt	CF_3	2-CN
86	H	COOEt	CF_3	2-Cl
87	H	COOH	CF_3	2-Cl,6-F
88	H	$CONH_2$	CF_3	2-Cl,6-F
89	H	CONHEt	CF_3	2-Cl,6-F
90	H	$CONEt_2$	CF_3	2-Cl,6-F
91	H	CONH	CF_3	2-Cl,6-F
101	CH_3	COOEt	CN	2-Cl,6-F
105	CH_3	COOMe	CN	2-Cl,6-F
106	CH_3	COOiPr	CN	2-Cl,6-F
107	CH_3	COOsecBu	CN	2-Cl,6-F
109	H	COOEt	CF_3	2-Cl,6-Cl

Further compound according to the invention are:

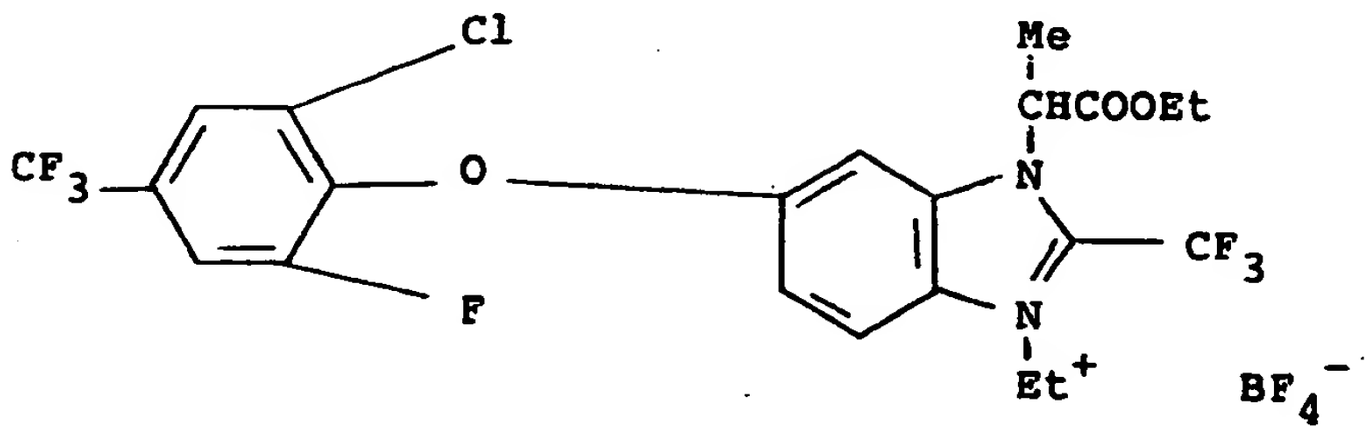
Compound 56



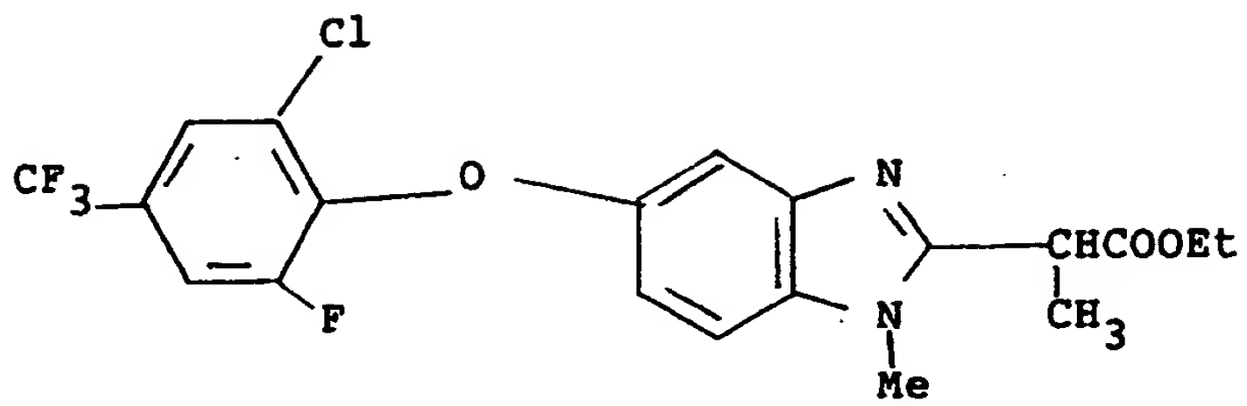
Compound 92



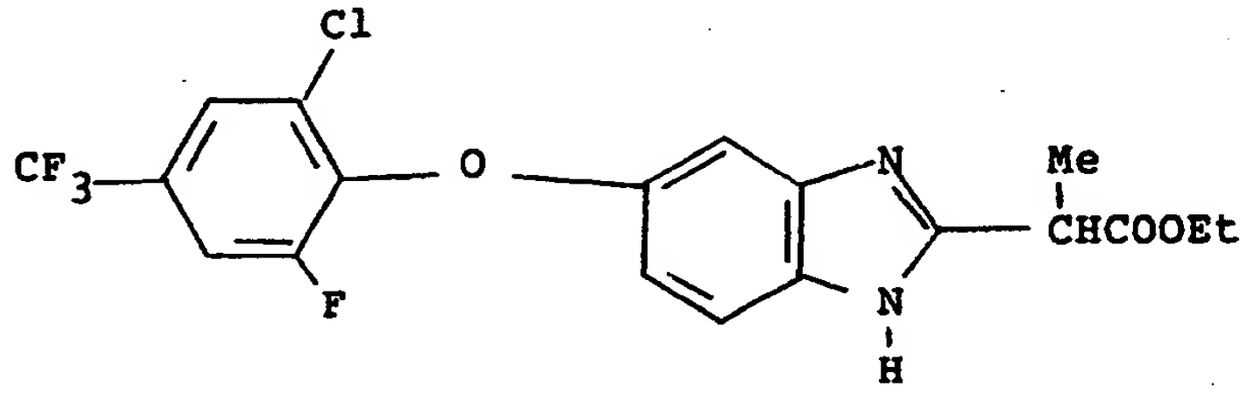
Compound 93



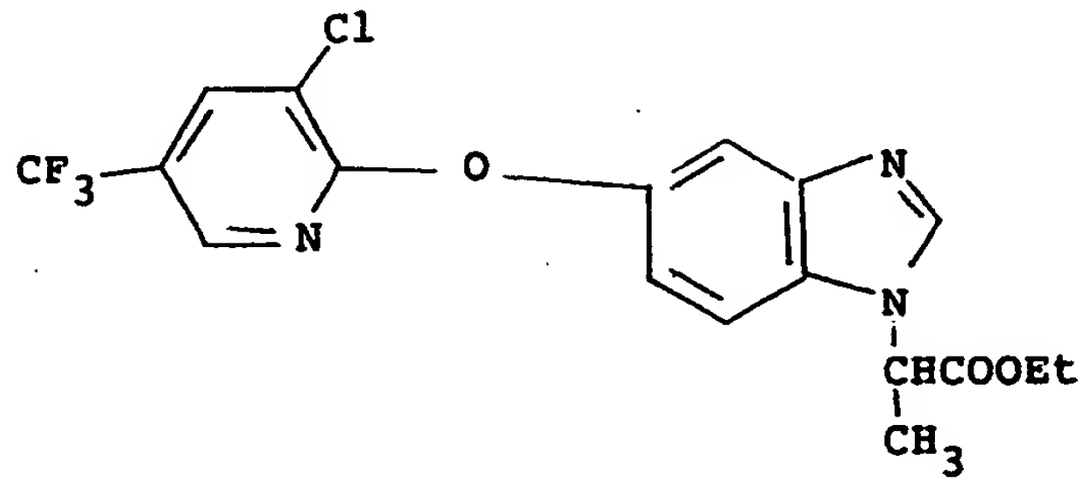
Compound 94



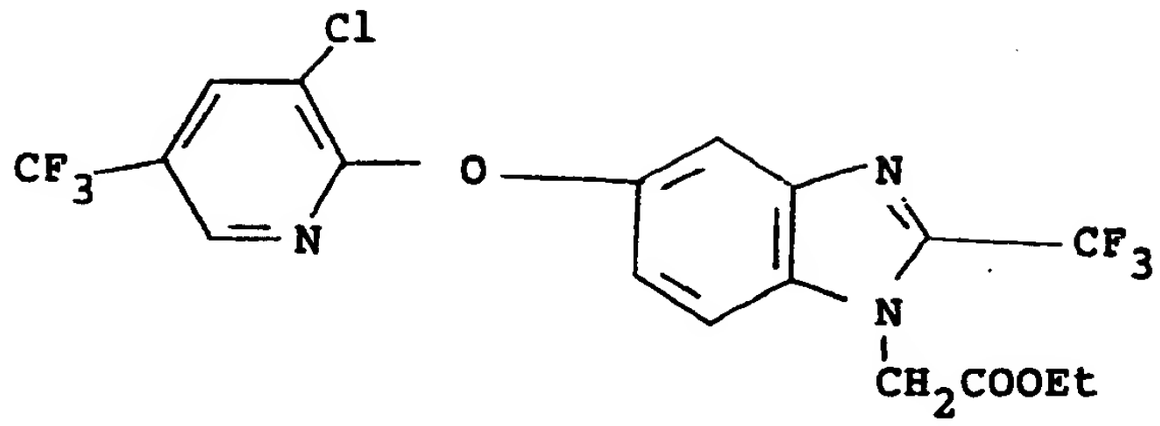
Compound 95



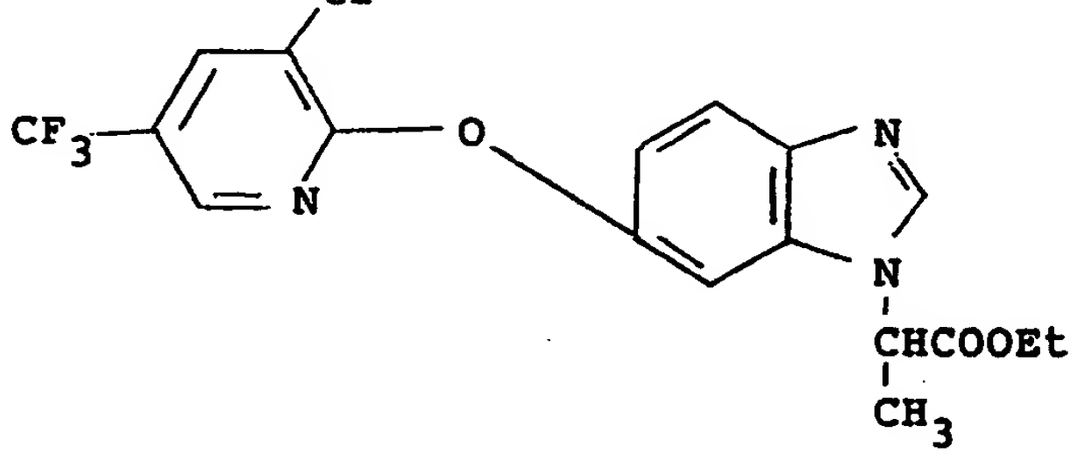
Compound 96



Compound 97



Compound 98



Compound 99

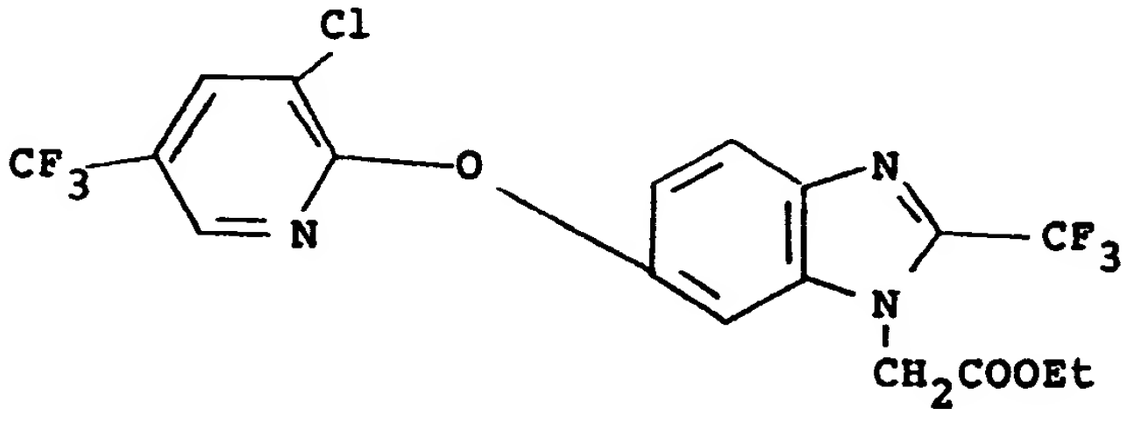


TABLE VI

Compound No.	Characterising Data (NMR)
1	$CDCl_3$:δ 1.15(t)3H; 1.88(d)3H; 4.14(q)2H; 5.18(q)1H; 6.77(s)1H; 6.86(dd)1H; 7.41(dd)1H; 7.61(s)1H; 7.68(d)1H; 8.0(s)1H.
2	$CDCl_3$:δ 1.22(t)3H; 4.19(t)2H; 5.04(s)2H; 6.70(s)1H; 6.86(dd)1H; 7.43(dd)1H; 7.61(s)1H; 7.69(d)1H; 8.01(s)1H.
3	DMSO:δ 1.51(d)3H; 5.41(q)1H; 6.88(dd)1H; 7.14(s)1H; 7.73(d)1H; 8.02(m)3H.
4	DMSO:δ 5.11(s)2H; 6.91(dd)1H; 7.17(s)1H; 7.75(d)1H; 8.01(m)3H.
5	$CDCl_3$:δ 3.73(s)3H; 5.07(s)2H; 6.71(s)1H; 6.86(dd)1H; 7.44(dd)1H; 7.62(s)1H; 7.69(d)1H; 8.01(s)1H.
6	$CDCl_3$:δ 1.11(t)3H; 1.88(d)3H; 4.13(q)2H; 5.15(q)1H; 6.65(s)1H; 6.80(dd)1H; 7.66(d)1H; 7.70(s)2H; 7.99(s)1H.
7	$CDCl_3$:δ 1.17(t)3H; 1.91(d)3H; 4.17(q)2H; 5.24(q)1H; 6.94(dd)1H; 7.07(d)1H; 7.15(s)1H; 7.70(dd)1H; 7.79(d)1H; 8.09(s)1H; 8.25(s)1H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
8	$CDCl_3$:δ 1.18(t)3H; 1.91(d)3H; 4.16(q)2H; 5.26(q)1H; 6.92(m)2H; 7.17(s)1H; 7.68(dd)1H; 7.81(d)1H; 7.95(s)1H; 8.09(s)1H.
9	$CDCl_3$:δ 1.16(t)3H; 1.89(d)3H; 4.15(q)2H; 5.21(q)1H; 6.89(dd)1H; 6.96(d)1H; 6.99(s)1H; 7.43(dd)1H; 7.73(m)2H; 8.04(s)1H.
10	$CDCl_3$: δ 1.89(d)3H; 3.68(s)3H; 5.20(q)1H; 6.78(s)1H; 6.84(dd)1H; 7.43(dd)1H; 7.61(s)1H; 7.68(d)1H; 8.01(s)1H.
11	$CDCl_3$: δ 0.74(t)3H; 1.50(m)2H; 1.89(d)3H; 4.02(t)2H; 5.18(q)1H; 6.78(s)1H; 6.84(dd)1H; 7.41(dd)1h; 7.60(S)1h; 7.68(d)1H; 8.00(s)1H.
12	$CDCl_3$: δ 0.80(t)3H; 1.15(m)3H; 1.45(m)2H; 1.89(d)3H; 4.06(t)2H; 5.16(q)1H; 6.78(s)1H; 6.84(dd)1H; 7.41(dd)1H; 7.61(s)1H; 7.67(d)1H; 8.00(s)1H.
13	$CDCl_3$: δ 1.15(t)3H; 1.86(d)3H; 4.15(q)2H; 4.09(q)1H; 6.71(s)1H; 6.90(dd)1H; 7.43(dd)1H; 7.63(m)2H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
14	$CDCl_3$: δ 1.15(t)3H; 1.89(d)3H; 4.15(q)2H; 5.20(q)1H; 6.81(m)2H; 7.70(d)1H; 7.90(s)1H; 8.01(m)2H.
15	$CDCl_3$: δ 1.14(t)3H; 1.88(d)3H; 4.13(q)2H; 5.17(q)1H; 6.78(m)2H; 7.67(d)1H; 8.03(m)2H; 8.18(s)1H.
16	$CDCl_3$: δ 1.14(t)3H; 1.88(d)3H; 4.13(q)2H; 5.19(q)1H; 6.81(m)2H; 7.71(d)1H; 7.95(s)1H; 8.02(s)1H; 8.17(s)1H.
17	$CDCl_3$: δ 1.14(t)3H; 1.87(d)3H; 4.14(q)2H; 5.19(q)1H; 6.78(dd)1H; 6.85(s)1H; 7.69(d)1H; 8.02(s)1H; 7.44(s)1H.
19	$CDCl_3$: δ 1.86(d)3H; 5.01(q)1H; 5.39(bs)1H; 6.34(bs)1H; 6.72(s)1H; 6.95(dd)1H; 7.45(dd)1H; 7.63(s)1H; 7.72(d)1H; 8.09(s)1H.
20	D6 DMSO: δ 1.66(d)3H; 3.52(s)9H; 5.35(q)1H; 6.93(dd)1H; 7.14(s)1H; 7.80(d)1H; 8.10(m)3H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
21	$CDCl_3$: δ 1.21(t)3H; 4.20(q)2H; 5.08(s)2H; 6.92(m)2H; 6.99(d)1H; 7.44(dd)1H; 7.75(m)2H; 8.06(s)1H.
22	$CDCl_3$: δ 1.26(t)3H; 4.22(q)2H; 5.10(s)2H; 6.95(dd)1H; 7.06(m)2H; 7.70(dd)1H; 7.80(d)1H; 8.08(s)1H; 8.25(s)1H.
23	$CDCl_3$: δ 1.26(t)3H; 4.22(q)2H; 5.12(s)2H; 6.95(m)3H; 7.12(s)1H; 7.69(dd)1H; 7.82(d)1H; 7.94(s)1H; 8.09(s)1H.
24	$CDCl_3$: δ 1.24(t)3H; 4.20(q)2H; 4.99(s)2H; 6.85(s)1H; 6.95(dd)1H; 7.03(d)1H; 7.48(dd)1H; 7.69(d)1H; 7.78(s)1H.
25	$CDCl_3$: δ 1.27(t)3H; 4.12(q)2H; 5.04(s)2H; 7.00(dd)1H; 7.04(s)1H; 7.10(d)1H; 7.74(d)2H; 8.28(s)1H.
26	$CDCl_3$: δ 1.27(t)3H; 4.13(q)2H; 5.04(s)2H; 6.93(d)1H; 7.02(dd)1H; 7.09(s)1H; 7.70(dd)1H; 7.76(d)1H; 7.95(s)1H.
27	D6DMSO: δ 5.12(s)2H; 7.00(dd)1H; 7.22(s)1H; 7.62(d)1H; 7.98(m)2H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
28	$CDCl_3$: δ 3.74(s)3H; 4.99(s)2H; 6.66(d)1H; 6.91(dd)1H; 7.44(dd)1H; 7.64(s+d)2H.
29	$CDCl_3$: δ 0.82(t)3H; 1.58(m)2H; 4.09(t)2H; 4.97(s)2H; 6.65(s)1H; 6.91(dd)1H; 7.43(dd)1H; 7.63(s+d)2H.
30	$CDCl_3$: δ 0.86(t)3H; 1.25(m)3H; 1.54(m)3H; 4.12(q)2H; 4.98(s)2H; 6.66(s)1H; 6.91(dd)1H; 7.44(dd)1H; 7.64(s+d)2H.
31	$CDCl_3$:δ 1.22(t)3H; 4.19(q)2H; 4.96(s)2H; 6.66(s)1H; 6.91(dd)1H; 7.43(dd)1H; 7.62(s+d)2H.
32	$CDCl_3$:δ 1.75(d)6H; 1.80(d)2.4H; 2.48(s)6H; 5.01(q)0.8H; 5.71(q)02H; 6.11(s)0.2H; 6.69(s)0.8H; 6.87(dd)0.2H; 6.97(dd)0.8H; 7.46(dd)1H; 7.62(s)1H; 7.66(d)0.2H; 7.73(d)0.8H; 8.0(s)0.2H; 8.09(s)0.8H.
33	$CDCl_3$:δ 1.24(t)3H; 1.89(d)3H; 4.19(q)2H; 5.27(q)1H; 6.78(s)1H; 7.01(dd)1H; 7.39(dd)1H; 7.59(s)1H; 7.68(d)1H; 8.04(s)1H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
34	$CDCl_3$: δ 1.28(t)3H; 4.25(q)2H; 5.11(s)2H; 6.78(s)1H; 7.0(dd)1H; 7.40(dd)1H; 7.59(s)1H; 7.67(d)1H; 7.99(s)1H.
35	$CDCl_3$:δ 1.90(d)3H; 3.73(s)3H; 5.29(q)1H; 7.01(dd)1H; 7.40(dd)1H; 7.59(s)1H; 7.66(d)1H; 8.03(s)1H.
36	d6 DMSO: δ 1.69(d)3H; 5.28(q)1H; 6.77(s)1H; 6.91(dd)1H; 7.75(d)1H; 7.99(s+d)2H; 8.41(s)1H.
37	$CDCl_3$:δ 1.16(t)3H; 1.80(d)3H; 4.16(q)2H; 5.26(q)1H; 6.98(dd)1H; 7.24(s)1H; 7.78(d)1H; 8.0(s)1H; 8.06(s)1H; 8.26(s)1H.
38	$CDCl_3$: δ 1.25(t)3H; 4.21(q)2H; 5.12(s)2H; 7.00(dd)1H; 7.18(s)1H; 7.80(d)1H; 8.02(s)1H; 8.09(s)1H; 8.27(s)1H.
39	$CDCl_3$: δ 1.24(t)3H; 4.21(q)2H; 5.04(s)2H; 7.05(dd)1H; 7.15(s)1H; 7.74(d)1H; 8.0(s)1H; 8.25(s)1H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
40	d6DMSO: δ 1.64(d)3H; 5.61(q)1H; 7.05(dd)1H; 7.28(d)1H; 7.66(d)1H; 8.04(m)2H.
41	D_2O: δ 1.52(d)1H; 4.80(q)1H; 6.60(dd)1H; 6.68(s)1H; 7.33(d)1H; 7.45(d)1H; 7.48(s)1H; 7.84(s)1H.
42	$CDCl_3$:δ 1.86(d)3H; 3.68(s)3H; 5.11(q)1H; 6.72(s)1H; 6.89(dd)1H; 7.43(dd)1H; 7.62(m)2H.
43	$CDCl_3$: δ 1.10(dd)6H; 4.98(m)1H; 5.06(q)1H; 6.70(d)1H; 6.91(dd)1H; 7.42(dd)1H; 7.62(m)2H.
44	$CDCl_3$: δ 0.80(t)3H; 1.15(m)2H; 1.46(m)2H; 1.87(d)3H; 4.06(t)2H; 5.09(q)1H; 6.72(d)1H; 6.89(dd)1H; 7.44(dd)1H; 7.62(m)2H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
45	$CDCl_3$: δ 0.74(t)3H; 1.50(m)2H; 1.88(d)3H; 4.03(t)2H; 5.10(q)1H; 6.71(d)1H; 6.90(dd)1H; 7.43(dd)1H; 7.62(m)2H.
46	$CDCl_3$: δ 1.88(d)3H; 3.25(s)3H; 3.48(m)2H; 4.24(m)2H; 5.15(q)1H; 6.75(s)1H; 6.89(dd)1H; 7.44(d)1H; 7.61(m)2H.
47	$CDCl_3$: δ 1.56(s)3H; 1.96(s+d)6H; 5.23(q)1H; 6.76(d)1H; 6.92(dd)1H; 7.44(dd)1H; 7.63(m)2H.
48	$CDCl_3$: δ 1.14(t)3H; 1.86(d)3H; 4.13(q)2H; 5.08(q)1H; 6.60(d)1H; 6.85(dd)1H; 7.63(d)1H; 7.72(s)2H.
49	$CDCl_3$: δ 1.20(t)3H; 1.91(d)3H; 1.16(q)2H; 5.18(q)1H; 6.94(d)1H; 6.99(dd)1H; 7.15(s)1H; 7.71(dd)1H; 7.76(d)1H; 7.96(s)1H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
50	$CDCl_3$: δ 1.14(t)3H; 1.86(d)3H; 4.14(q)2H; 5.10(q)1H; 6.76(d)1H; 6.85(dd)1H; 7.65(d)1H; 7.91(s)1H; 8.00(d)1H.
51	$CDCl_3$: δ 2.01(d)3H; 5.45(q)1H; 6.88(m)2H; 7.43(dd)1H; 7.62(s)1H; 7.69(q)4H; 7.72(d)1H; 8.06(s)1H.
52	$CDCl_3$: δ 1.50(s)3H; 1.92(s)3H; 1.98(d)3H; 5.30(q)1H; 6.80(s)1H; 6.86(dd)1H; 7.42(dd)1H; 7.61(s)1H; 7.68(d)1H; 8.01(s)1H.
53	$CDCl_3$: δ 1.86(d)3H; 5.11(q)1H; 6.62(d)1H; 6.86(dd)1H; 7.62(d)1H; 7.72(s)2H.
54	$CDCl_3$: δ 1.92(d)3H; 5.22(q)1H; 6.94(d)1H; 6.99(dd)1H; 7.13(s)1H; 7.72(dd)1H; 7.75(d)1H; 7.96(d)1H.
55	$CDCl_3$: δ 1.89(d)3H; 5.14(q)1H; 6.76(s)1H; 6.86(dd)1H; 6.65(d)1H; 7.90(s)1H; 8.00(s)1H.
56	D6DMSO: δ 1.54(d)3H; 3.14(s)3H; 5.39(q)1H; 6.86(dd)1H; 7.08(s)1H; 7.73(d)1H; 7.98(m)2H; 8.05(s)1H.

TABLE VI (Cont/d)

Compound No.	Characterising Data (NMR)
61	$CDCl_3$: δ1.18(t)3H; 1.82(d)3H; 4.20(q)2H; 5.35(q)1H; 7.19(m)2H; 7.39(m)2H; 7.60(s)1H.
62	$CDCl_3$: δ1.15(t)3H; 1.75(d)3H; 2.6(s)3H; 4.15(q)2H; 5.05(q)1H; 6.8(dd)1H; 6.9(d)1H; 7.4(dd)1H; 7.6(d+s)2H.
63	$CDCl_3$: δ1.2(t)3H; 1.85(d)3H; 2.65(s)3H; 4.2(q)2H; 5.1(q)1H; 6.85(d)1H; 6.95(dd)1H; 7.3(d)1H; 7.4(dd+d)2H; 7.7(s)1H.
64	$CDCl_3$: δ(1.25(t)3H; 1.95(d)3H; 4.25(q)2H; 5.15(q)1H; 7.0(d)1H; 7.1(dd)1H; 7.45(d)1H; 7.55(d)1H; 7.65(dd)1H; 8.15(s)1H; 8.25(d)1H.
65	$CDCl_3$: δ(1.4(t)3H; 2.05(d)1H; 4.35(q)2H; 5.3(?)1H; 7.0(d)1H; 7.2(dd)1H; 7.6(d)1H; 7.7(d)1H; 7.8(dd)1H; 8.05(d)1H; 8.3(s)1H.
66	$CDCl_3$: δ1.25(t)3H; 1.9(d)3H; 4.2(q)2H; 5.15(q)1H; 6.9(d)1H; 7.05(dd)1H; 7.4(dd+d)2H; 7.5(d)1H; 7.75(d)1H; 8.15(s)1H.

TABLE VI (contd)

Compound No.	Characterising Data (NMR)
67	$CDCl_3$: δ1.25(t)3H; 1.9(d)2H; 4.2(q)2H; 5.1(q)1H; 7.05(dd+d)2H; 7.3(d)1H; 7.7(s)2H; 8.05(s)1H.
68	$CDCl_3$: δ1.3(t)3H; 4.25(q)2H; 5.1(s)2H; 7.1(dd)1H; 7.2(d)1H; 7.25(d)1H; 7.4(dd)1H; 7.6(s)1H; 7.9(s)1H.
69	$CDCl_3$: δ1.25(t)3H; 4.25(q)2H; 5.0(s)2H; 7.25(m)2H; 7.325(d)1H; 7.4(dd)1H; 7.0(s)1H.
70	$CDCl_3$: δ1.3(t)3H; 4.3(q)2H; 5.05(s)2H; 6.9(d)1H; 7.275(dd)1H; 7.45(d)1H; 7.7(m)2H; 7.95(d)1H.
71	$CDCl_3$: δ1.3(t)3H; 4.275(q)2H; 5.05(s)2H; 6.925(d)1H; 7.225(dd)1H; 7.4(m)2H; 7.525(d)1H; 7.75(d)1H.
72	$CDCl_3$ δ3.4-4.2(broad hump)1H; 5.0(s)2H; 5.0(s)2H; 7.225(m)2H; 7.4(m)2H; 7.6(s)1H.
73	m.p. 250.2-252.2°C. m^+ = 454

TABLE VI (contd)

Compound No.	Characterising Data (NMR)
74	$CDCl_3$: δ1.1(t)3H; 3.3(quintet)2H; 4.9(s)2H; 5.45(t)1H; 7.25(m)2H; 7.4(m)2H; 7.6(s)1H.
75	$CDCl_3$: δ1.13(t)3H; 1.80(d)3H; 4.18(q)2H; 5.30(q)1H; 6.95(m)2H; 7.40(dd)1H; 7.60(s)1H; 7.81(d)1H.
76	DMSO: δ1.60(d)3H; 5.38(q)1H; 7.04(dd)1H; 7.24(d)1H; 7.80(d)1H; 8.01(m)2H.
77	$CDCl_3$: δ1.2(t)3H; 1.8(d)3H; 2.6(s)3H; 4.2(q)2H; 5.01(q)1H; 7.25(d)1H; 7.04(dd)1H; 7.6(s)1H.
78	$CDCl_3$: δ1.2(t)3H; 1.8(d)3H; 2.65(t)3H; 4.2(q)2H; 5.1(q)1H; 6.85(d)1H; 6.95(dd)1H; 7.1(d)1H; 7.4(dd)1H; 7.7(d+s)2H.
79	$CDCl_3$: δ1.25(t)3H; 1.9(d)3H; 4.2(q)2H; 5.1(q)1H; 7.05(dd+d)2H; 7.2(d)1H; 7.7(dd)1H; 7.85(dd)1H; 8.15(s)1H; 8.25(d)1H.

TABLE VI (contd)

Compound No.	Characterising Data (NMR)
80	$CDCl_3$: δ1.25(t)3H; 1.9(d)3H; 4.2(q)2H; 5.1(q)1H; 6.9(d)1H; 7.05(dd)1H; 7.2(d)1H; 7.7(dd)1H; 7.85(d)1H; 7.95(d)1H; 8.15(s)1H.
81	$CDCl_3$: 1.25(t)3H; 1.9(d)3H; 4.2(q)2H; 5.05(q)1H; 6.9(d)1H; 7.0(dd)1H; 7.1(d)1H; 7.4(dd)1H; 7.75(d)1H; 7.85(d)1H; 8.1(s)1H.
82	$CDCl_3$: δ1.2(t)3H; 1.85(d)3H; 4.2(q)2H; 5.0(q)1H; 6.8(dd+d)2H; 7.7(m)1H; 8.05(s)1H.
83	$CDCl_3$: δ1.25(t)3H; 4.25(q)2H; 4.8(s)1H; 6.85(d)1H; 6.9(dd)1H; 7.4(dd)1H; 7.6(s)1H; 7.75(d)1H; 7.9(s)1H.
84	$CDCl_3$: δ1.25(t)3H; 4.25(q)2H; 4.95(s)2H; 6.85(d)1H; 7.0(dd)1H; 7.425(dd)1H; 7.6(s)1H; 7.85(d)1H.
85	$CDCl_3$: δ1.25(t)3H; 4.25(q)2H; 5.0(s)2H; 6.9(d)1H; 7.15(m)2H; 7.7(dd)1H; 7.95(m)2H.

TABLE VI (contd)

Compound No.	Characterising Data (NMR)
86	$CDCl_3$: δ1.25(t)3H; 4.25(q)2H; 4.975(s)2H; 6.95(d)1H; 7.025(d)1H; 7.125(dd)1H; 7.45(dd)1H; 7.75(d)1H; 7.9(d)1H.
87	$CDCl_3$: δ4.8-5.2(broad)1H; 4.9(s)2H; 6.875(d)1H; 7.0(dd)1H; 7.425(dd)1H; 7.6(s)1H; 7.825(d)1H.
88	Mass Spec. M^+=455 MH^+=456 m.p. 236.7-237.7°C
89	$CDCl_3$: δ1.05(t)3H; 3.25(q)2H; 4.85(s)2H; 5.45(t)1H; 6.875(d)1H; 7.1(dd)1H; 7.42(dd)1H; 7.6(s)1H; 7.85(d)1H.
90	$CDCl_3$: δ1.1(t)3H; 1.25(t)3H; 3.4(q)4H; 5.0(s)2H; 6.85(d)1H; 6.92(dd)1H; 7.4(dd)1H; 7.55(s)1H; 7.8(d)1H.
91	$CDCl_3$: δ(5.025(s)2H; 6.95(m)2H; 7.1(t)1H; 7.3(m)3H; 7.47(d)2H; 7.55(s)1H; 7.8(d)1H; 9.35(s)1H.
92	m.p. 166.1-167.5°C

TABLE VI (contd)

Compound No.	Characterising Data (NMR)
93	m.p. 135-136.1°C
94	m.p. 123.2-128.6°C
95	$CDCl_3$: δ1.1(t)3H; 1.5(d)3H; 3.95-4.2(m)3H; 6.9(dd)1H; 7.0(d)1H; 7.5(d)1H; 7.95(d+s)2H.
96	$CDCl_3$: δ1.25(t)3H; 1.9(d)3H; 4.2(q)2H; 5.15(q)1H; 7.15(dd)1H; 7.45(d)1H; 7.65(d)1H; 8.00(d)1H; 8.15(s)1H; 8.25(d)1H.
97	$CDCl_3$: δ1.25(t)3H; 4.25(q)2H; 5.05(s)2H; 7.3(dd)1H; 7.425(d)1H; 7.725(d)1H; 8.0(d)1H; 8.25(s)1H.
98	$CDCl_3$: δ1.25(t)3H; 1.9(d)3H; 4.2(q)2H; 5.1(q)1H; 7.1(dd)1H; 7.25(d)1H; 7.85(d)1H; 8.0(d)1H; 8.15(s)1H; 8.25(s)1H.
99	$CDCl_3$: δ1.25(t)3H; 4.2(q)2H; 5.0(s)2H; 7.2(m)2H; 7.95(d)1H; 8.0(d)1H; 8.25(s)1H.

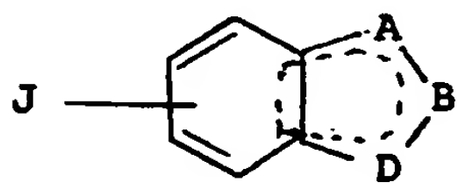
TABLE VI (contd)

Compound No.	Characterising Data (NMR)
100	$CDCl_3$: δ1.25(t)3H; 1.95(d)3H; 4.25(q)2H; 5.4(q)1H; 7.15(d)1H; 7.27(dd)1H; 7.44(ddx2)2H; 7.62(s)1H.
101	$CDCl_3$: δ1.25(t)3H; 1.9(d)3H; 4.25(q)2H; 5.35(q)1H; 6.92(d)1H; 7.02(dd)1H; 7.62(s)1H; 7.45(dd)1H; 7.8(d)1H.
102	$CDCl_3$: δ1.95(d)3H; 3.8(S)3h; 5.45(Q)1h; 7.15(D)1h; 7.2(DD)1h; 7.45(D)2h; 7.63(S)1h.
103	$CDCl_3$: δ1.17(d)3H; 1.28(d)3H; 1.95(d)3H; 5.1(q)1H; 5.35(q)1H; 7.15(d)1H; 7.25(dd)1H; 7.42(d)2H; 7.63(s)1H.
104	$CDCl_3$: δ 3.85(s)3H; 5.1(s)2H; 7.18(s)1H; 7.3(d)2H; 7.45(dd)1H; 7.63(s)1H.
105	$CDCl_3$: δ 1.93(d)3H; 3.8(s)3H; 5.35(q)1H; 6.93(d)1H; 7.02(dd)1H; 7.45(dd)1H; 7.63(s)1H; 7.8(d)1H.

TABLE VI (contd)

Compound No.	Characterising Data (NMR)
106	$CDCl_3$: δ 1.15(d)3H; 1.25(d)3H; 1.9(d)3H; 5.06(q)1H; 5.3(q)1H; 6.9(d)1H; 7.03(dd)1H; 7.45(d)1H; 7.63(s)1H; 7.8(d)1H.
107	$CDCl_3$: δ (0.85+0.65 2x t) 3H; 1.1-1.2(2xd)3H; 1.4-1.6(m)2H; 1.9(q)3H; 4.9(m)1H; 5.3(q)1H; 6.9(m)1H; 7.02(m)1H; 7.45(dd)1H; 7.65(s)1H; 7.8(d)1H.
108	$CDCl_3$: δ 1.3(t)3H; 4.3(q)2H; 5.08(s)2H; 7.02(d)1H; 7.25(dd)1H; 7.45(d)1H; 7.65(d)1H;7.77(dd)1H; 8.35(d)1H.
109	$CDCl_3$: δ 1.25(t)3H; 4.2(q)2H; 4.9(s)2H; 6.8(d)1H; 6.95(dd)1H; 7.7(s)2H; 7.82(d)1H.

Compounds of formula (I) may be prepared by the following general processes:
a) reacting a compound of formula (II'):



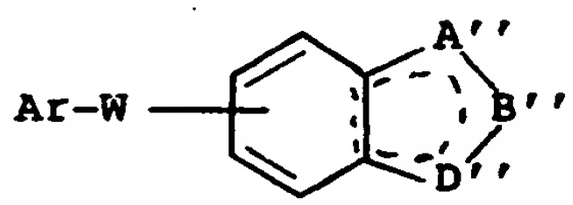
(II')

where A, B and D are as defined in relation to formula (I) and J is OH or CF_3CONH with a compound of formula (III):

Ar-Z (III)

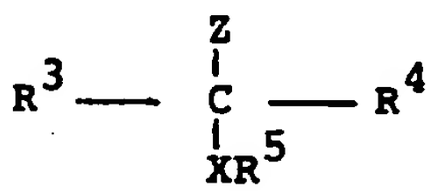
where Ar is as defined in relation to formula (I) and Z is a leaving group, optionally in the presence of a base; or

b) reacting a compound of formula (XXXXI):



(XXXXI)

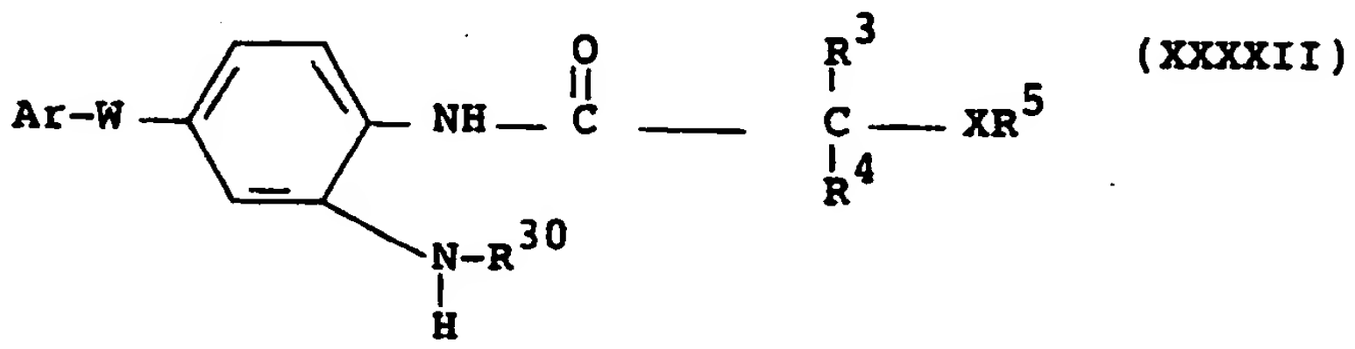
where Ar and W are as defined in relation to formula (I) and A'', B'' and D'' are independently selected from N, NR^2 , NH, CR^6, CH or CHR^6; provided 2 of A'', B'' and D'' are N, NR^2 or NH and at least one of A, B or D carries a hydrogen atom with a compound of formula (VII):



(VII)

where X, R^3 , R^4 and R^5 are as defined in relation to formula (I) and Z is a leaving group in an organic solvent in the presence of a base; or

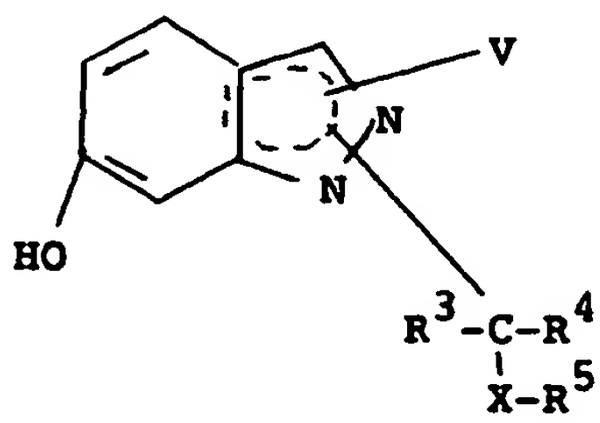
c) cyclisation of compounds of formula (XXXXII):



(XXXXII)

wherein Ar, W, X, R^3 , R^4 and R^5 are as defined in relation to formula (I) and R^{30} is H or lower alkyl in the presence of a dehydrating agent. Further details for these general processes are set out below.

Compounds of formula (IA) may be prepared by reacting a compound of formula (II):



(II)

wherein V, X, R^3, R^4 and R^5 are as defined in relation to formula (IA) with a compound of formula (III) :

Ar-Z (III)

wherein Ar is as defined in relation to formula (I) and Z is a leaving group, optionally in the presence of a base.

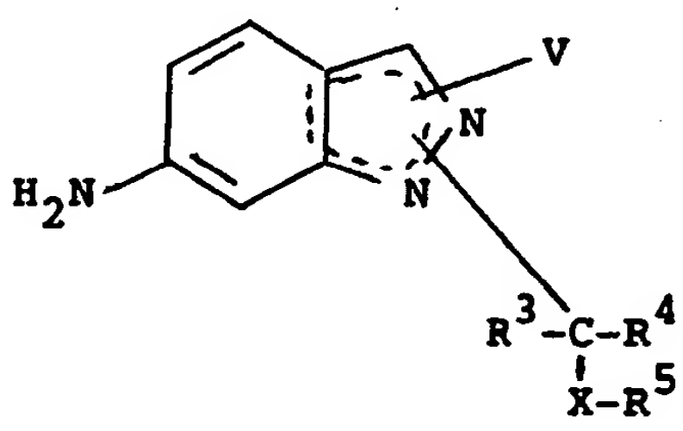
Suitable leaving groups Z include halide, such as fluoride, bromide and chloride, and sulphonates such as methanesulphonate and p-toluenesulphonate.

Suitable bases for use in the reaction include bases such as sodium hydride, and alkali metal carbonates and hydroxides.

The reaction is preferably carried out in an organic solvent such as dimethylformamide, dimethylsul-

phoxide, a lower alkanol, or a lower ketone. Moderate temperatures, for example of from 20° to 120°C are suitably employed. Conveniently the reaction is carried out at 100° to 110°C.

Compounds of formula (II) can be prepared from compounds of formula (IV) :



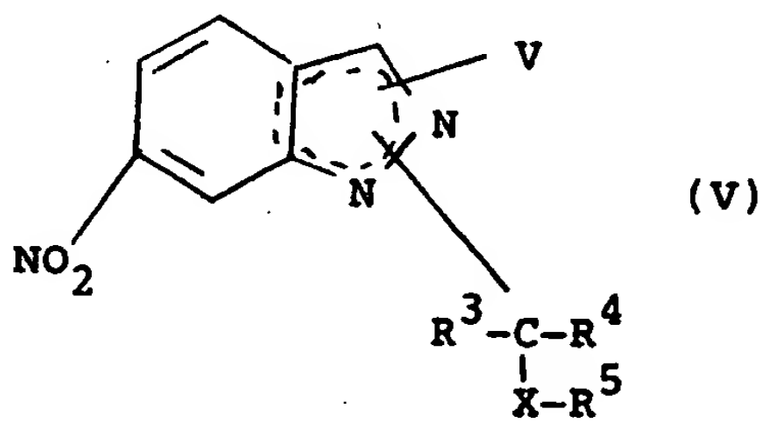
(IV)

wherein V, X, R^3, R^4 and R^5 are as defined in relation to formula (IA), by diazotisation with nitrous acid followed by aqueous acidic hydrolysis e.g. according to the procedure described in J. Org. Chem (1977), 42(12), 2053.

Alternatively compounds of formula (II) where V is other than cyano can be prepared from compounds of formula (IV) by reaction with water and sulphuric acid at 150-170°C and 100-120 psi; e.g. according to the procedure described in J.C.S. (1955) 2412.

Compounds of formula (II) are novel and as such form a further aspect of the invention.

Compounds of formula (IV) are prepared by reduction of the corresponding nitro compound of formula (V) where V, X, R^3, R^4 and R^5 are as defined in relation to formula (IA).

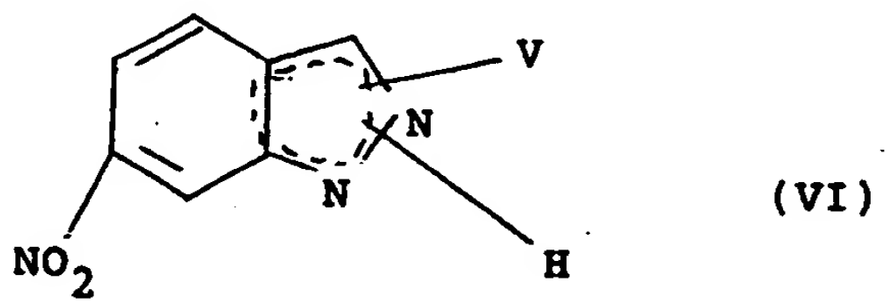


(V)

A wide variety of reducing agents may be used and may be selected form the chemical literature by the skilled worker in the art. The reduction may be carried out for example by using sodium dithionite or tin and hydrochloric acid, iron and hydrochloric acid, reduced iron with hydrochloric acid in isopropanol or hydrogen with a palladium on charcoal catalyst. The reaction is preferably effected in an organic solvent such as a lower alkyl alcohol optionally mixed with water at temperatures of from 20°C to 90°C.

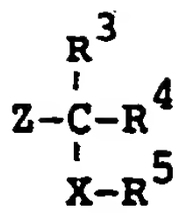
Compounds of formula (IV) are novel and as such form a further aspect of the invention.

Compounds of formula (V) can be prepared from compounds of formula (VI) :



(VI)

by reaction with compounds of formula (VII) :



(VII)

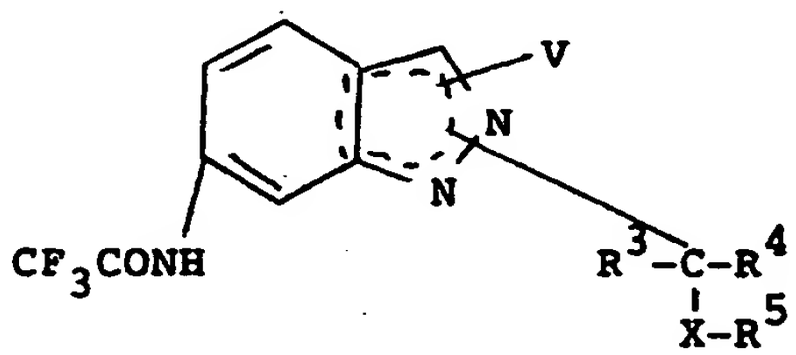
wherein X, R^3, R^4 and R^5 are as defined in relation to formula (IA) and Z is a leaving group as hereinbefore defined in solvents such as dimethylformamide, dimethylsulphoxide or lower alkyl ketones in the presence of a base such as sodium hydride, alkali metal carbonates or hydroxides at temperatures from 20° to 80° C.

Compounds of formula (V) are novel and as such form a further aspect of the invention.

Compounds of formula (III), (VI) and (VII) are known compounds or they can be prepared from known compounds by known methods.

Compounds of formula (IA) where the Ar-W is attached at positions other than the 6 position of the indazole ring may be made starting from the appropriate nitro analogue of compounds of formula (VI). These analogues may be prepared using methods known in the art.

Compounds of formula (IA) where W is NH may be prepared by reacting a compound of formula (VIII) :



(VIII)

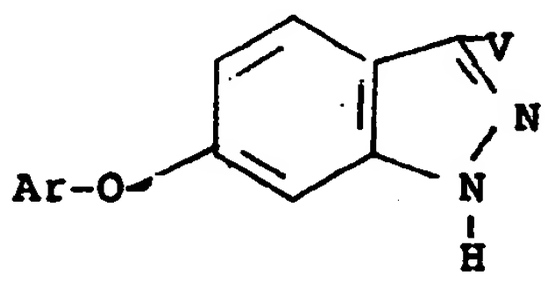
wherein X, R^3, R^4 and R^5 are as defined in relation to formula (I) with sodium hydride in dimethylformamide or dimethylsulphoxide and reacting the anion so formed with a compound of formula (III) as herebefore defined in dimethylformamide or dimethylsulphoxide at temperatures of from 50° to 90° C.

Compounds of formula (VIII) may be prepared from compounds of formula (IV) as hereinbefore defined by reaction with trifluoroacetic anhydride according to the procedure desribed in J. Org. Chem., 1965, 30, 1287.

Compounds of formula (VIII) are novel and as such form a further aspect of the invention.

Compounds of formula (IA) produced by the foregoing method may be alkylated by standard techniques to produce compounds of formula (IA) where W is NR^1.

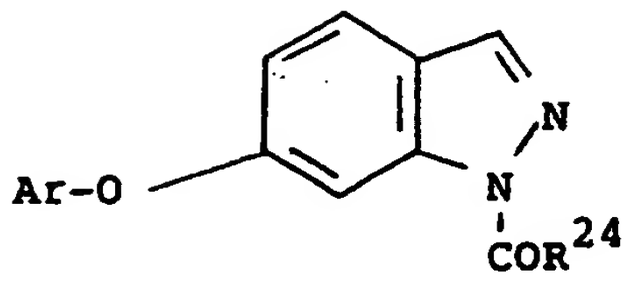
Compounds of formula (IA) where V is H attached to the carbon atom at the 3 position of the indazole and W is oxygen attached to the indazole ring at the 6 position may be prepared from compounds of formula (IX):



(IX)

where Ar is as defined in relation to formula (IA) by reaction with a compound of formula (VII) as hereinbefore defined in solvents such as dimethylformamide, dimethylsulphoxide, lower alkanols, lower alkanones at temperatures of from 60-100° C in the presence of a base such as sodium hydride, alkali metal carbonates or hydroxides.

Compounds of formula (IX) are prepared by deacylation of compounds of formula (X):

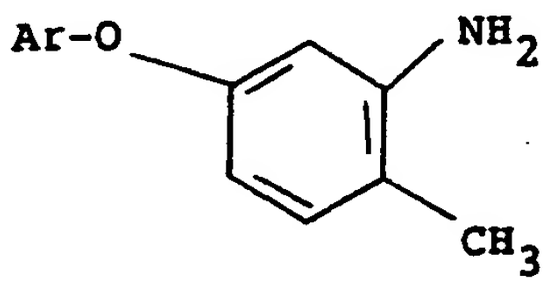


(X)

where R^{24} is lower alkyl and Ar is as defined in relation to formula (IA).

Compounds of formula (IX) are novel and as such form a further aspect of the invention.

Compounds of formula (X) are prepared from compounds of formula (XI):

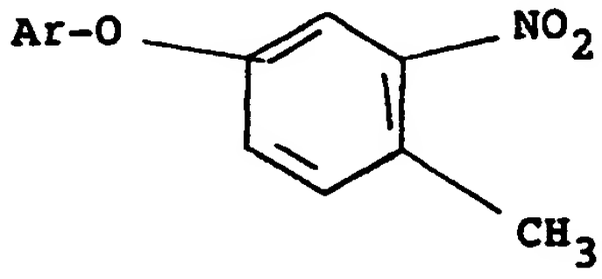


(XI)

by a Jacobsen reaction (C. Ruchardt and V. Hassmann, Synthesis, 375, 1972 and F. Trondlin, R. Werner and C. Ruchardt Ber., 367, 111, 1978) using solvents such as benzene or toluene at temperatures of from 80-110° C.

Compounds of formula (X) are novel and as such form a further aspect of the invention.

Compounds of formula (XI) are prepared by reduction of compounds of formula (XII).



(XII)

A wide variety of reducing agents may be used and may be selected form the chemical literature by the skilled worker in the art. The reduction may be carried out for example by using sodium dithionite or tin and hydrochloric acid, iron and hydrochloric acid, reduced iron with hydrochloric acid in isopropanol, or hydrogen with a palladium on charcoal catalyst. The reaction is preferably effected in an organic solvent such as a lower alkyl alcohol optionally mixed with water at temperatures of from 20° C to 90° C.

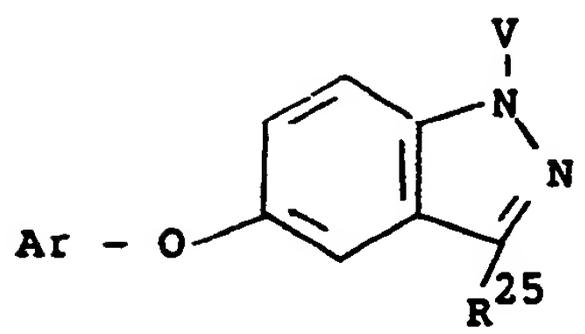
Compounds of formula (XI) other than 4-(2,4-dichlorophenoxy)-2-methylaniline are novel and as such form a further aspect of the invention.

Compounds of formula (XII) are prepared by reacting a compound of formula (III) as hereinbefore defined with the known compound 4-methyl-3-nitrophenol in solvents such as dimethylformamide, dimethylsulphoxide or lower alkanones at temperatures of 90-120° C in the presence of a base such as sodium hydride, alkaline metal carbonates and hydroxides.

Compounds of formula (XII) other than 4-(2,4-dichlorophenoxy)-2-methylnitrobenzene are novel and as such form a further aspect of the invention.

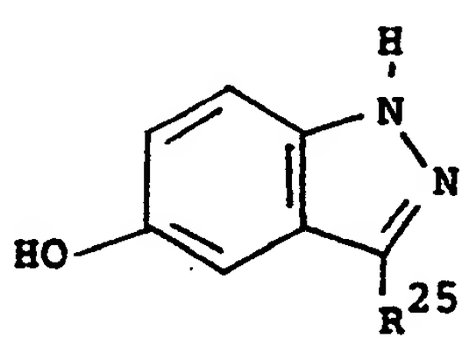
The corresponding 5-aryloxy indazoles may be produced by an analogous process using appropriate starting materials.

Compounds of formula (IB):



(IB)

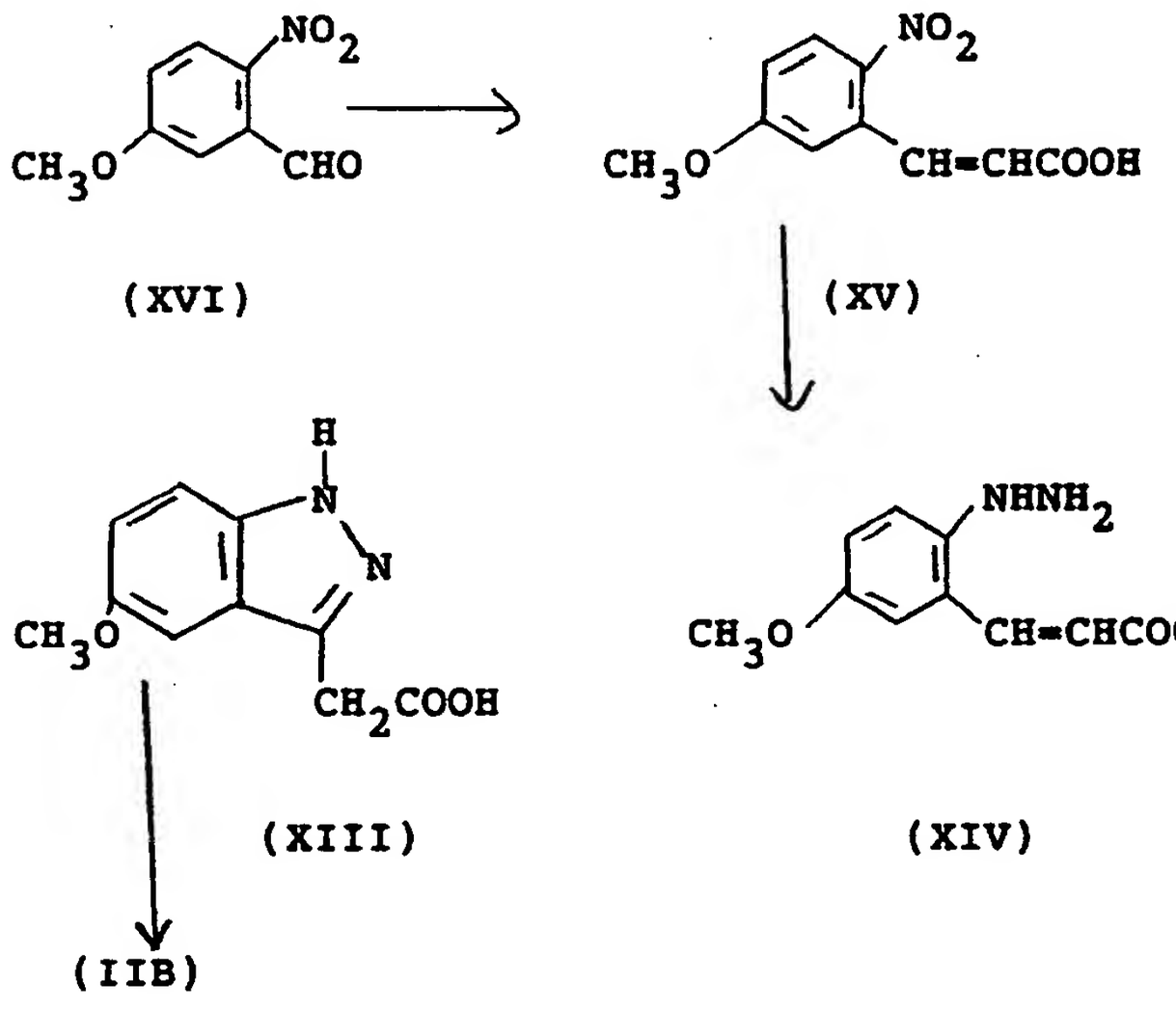
where Ar, and V, are as defined in relation to formula (IA) except V is not haloalkyl and R^{25} is CH_2COOR^{11} or $CH(CH_3)COOR^{11}$ where R^{11} is as defined in relation to formula (IA) may be prepared from a compound of formula (IIB)



(IIB)

by reaction with compound of formula (III) as described above in the reaction of compounds of formula (II) with formula (III).

The compound of formula (IIB) is prepared for example by the method of Fucher and Tafel Ann. 303, 227, 1885 as shown in the following scheme:



The compound of formula (IIB), may be prepared by demethylation of a compound of formula (XIII) using for example boron tribromide at -70 to -50 °C in dichloromethane optionally followed by esterification with the appropriate R^{11} alcohol.

The compound of formula (XIII) may be formed by cyclisation of a compound of formula (XIV) by reaction with air at 0 - 20 °C in aqueous sodium or potassium hydroxide solution.

The compound of formula (XIV) may be prepared by reduction of a compound of formula (XV) to its corresponding amine, diazotisation using sodium nitrite and concentrated hydrochloric acid followed by a

further reduction of the diazonium compound with for example stannous chloride in hydrochloric acid or sodium sulphite and sulphur dioxide.

The compound of formula (XV) may be prepared from a compound of formula (XVI) by reaction with sodium acetate and acetic anhydride at 150-180 °C.

The compound of formula (XVI) is a known compound.

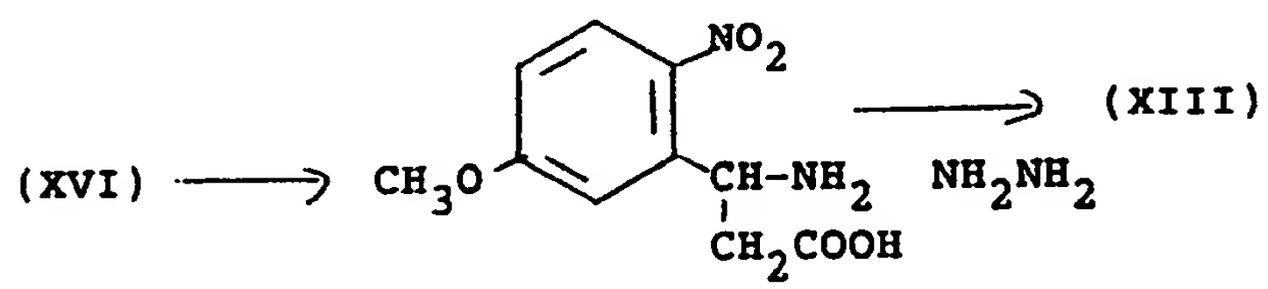
The scheme as shown produces compounds of formula (IB) where V is H. Further compounds of formula (IB) where V is other than H may be produced by standard methods. For example treatment of a compound of formula (IB) where V is H with a lower alkyl halide such as methyl iodide, or a lower alkyl sulphate such as dimethyl sulphate or diethyl sulphate would yield compounds where V is lower alkyl.

Alternatively treatment with a lower alkyl haloformate such as ethyl chloroformate would yield compounds of formula (IB) where V is COO-lower alkyl.

The scheme as shown also produces compounds of formula (IB) where R^{25} is CH_2COOR^{11}. The treatment of these compounds with a base e.g. potassium t-butoxide, potassium or lithium bis-(trimethylsilyl)amide at temperatures from 0 to -40 °C in THF with methyl iodide would yield the corresponding compounds of formula (IB) where R^{25} is $CH(CH_3)COOR^{11}$.

The corresponding 6-aryloxyindazoles may be produced by an analogous process using appropriate starting materials.

An alternative method of preparing compounds of formula (XIII) is the method of Kariyone and Yagi C.A. 186340j, 93, 1980 as shown in the following scheme:

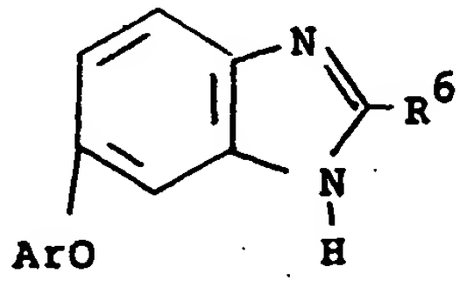


(XVII)

The compound of formula (XIII) may be prepared from a compound of formula (XVII) by reaction with activated charcoal and hydrazine hydrate in aqueous sodium hydroxide at 30 to 80 °C.

The compound of formula (XVII) may be prepared from a compound of formula (XVI) as hereinbefore defined by reaction with malonic acid and ammonium formate in formic acid at 40 to 95 °C.

Compounds of formula (IC) where W is oxygen, A is N, B is CR^6 and D is $NCR^3R^4XR^5$ may be prepared by reacting a compound of formula (XVIII) :

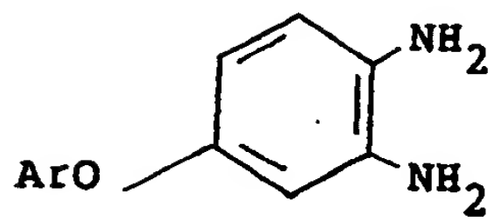


(XVIII)

wherein Ar and R^6 are as defined in relation to formula (IC) with a compound of formula (VII) as hereinbefore defined in a suitable solvent e.g. dimethylsulphoxide, dimethylformamide, acetonitrile, a lower alkyl ketone in the presence of an appropriate base e.g. sodium hydride, alkyl metal carbonate at 50-100 °C.

This reaction produces two regio-isomers which may be readily separated by known techniques (e.g. chromatography or preparative tlc) to produce two compounds of formula (IC).

Compounds of formula (XVIII) can be prepared by cyclisation of compounds of formula (XIX) :

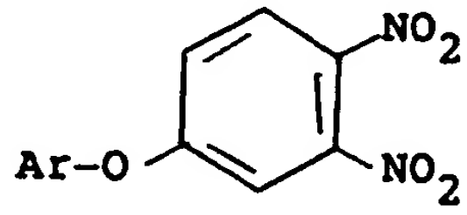


(XIX)

wherein Ar is as defined in relation to formula (IC), using an appropriate organic, aliphatic acid at 100-120°C with or without aqueous mineral acid e.g. hydrochloric acid.

Compounds of formula (XVIII) are novel and as such form a further aspect of the invention.

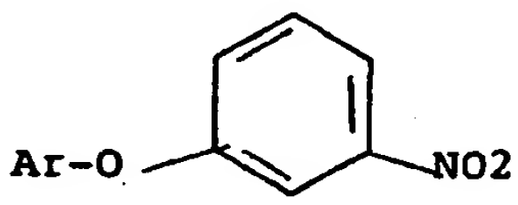
Compounds of formula (XIX) are prepared by reduction of the corresponding dinitro compound of formula (XX) :



(XX)

A wide variety of reducing agents may be used and may be selected from the chemical literature by the skilled worker in the art. The reduction may be carried out for example by using sodium borohydride with a palladium on charcoal catalyst. The reaction is preferably effected in an organic solvent such as a lower alcohol optionally mixed with water at temperatures of from -20°C to 10°C.

Compounds of formula (XX) can be prepared by nitration of a compound of formula (XXI) :



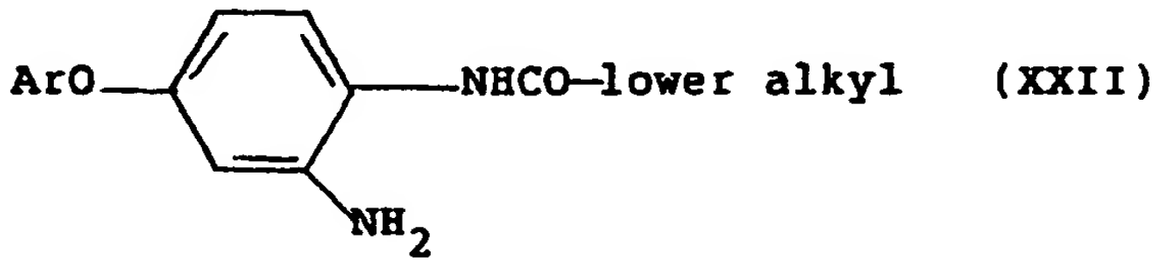
(XXI)

using a nitrating agent such as potassium nitrate mixed with concentrated sulphuric acid. The reaction is preferably carried out in a suitable solvent such as acetic anhydride, methylene dichloride, ethylene dichloride or concentrated sulphuric acid. Temperatures of from -20°C to 25°C are suitably employed.

Compounds of formula (XXI) are prepared by reacting m-nitrophenol with a compound of formula (III) as hereinbefore defined in an organic solvent, for example dimethylsulphoxide, lower alkyl ketones such as acetone or butanone, lower glymes e.g. $MeOCH_2CH_2OMe$ in the presence of a base e.g. alkaline metal hydroxides (KOH) or carbonates (K_2CO_3) at a temperature of 50 to 120°C.

If it is desired to produce a compound of formula (IC) where the ArW is attached at other positions on the carbocyclic portion of the benzimidazole ring, the appropriate dinitro analogue of a compound of formula (XX) would be employed. These may be produced from known starting materials by methods known in the art.

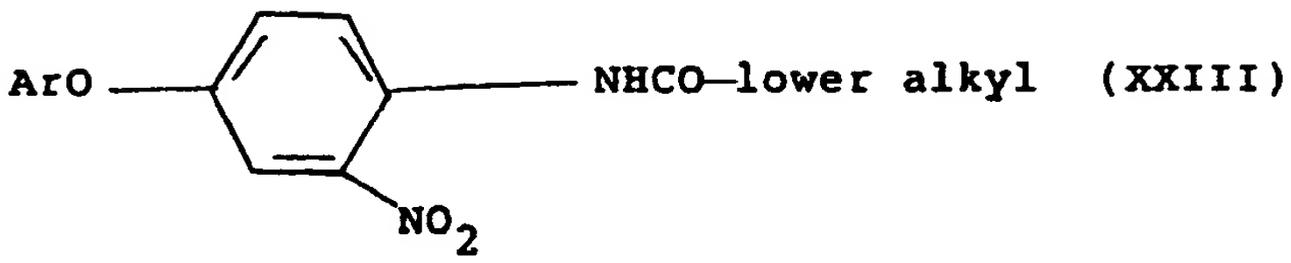
Compounds of formula (XVIII) may alternatively be prepared from compounds of formula (XXII):



(XXII)

where Ar is as defined in relation to formula (IC) by heating in the approprate lower aliplatic acid at 100-120°C.

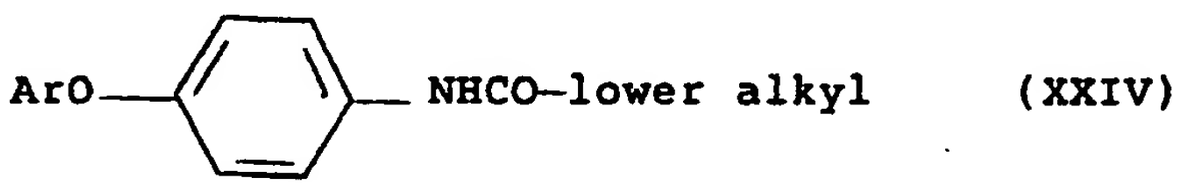
Compounds of formula (XXII) may be prepared by reduction of compounds of formula (XXIII):



(XXIII)

where Ar is as defined in relation to formula (IC) using a wide variety of reducing agents which may be selected from the chemical literature by those skilled in the art. The reduction may be carried out for example by using titanium trichloride in aqueous hydrochloric acid at 0° to 10° C.

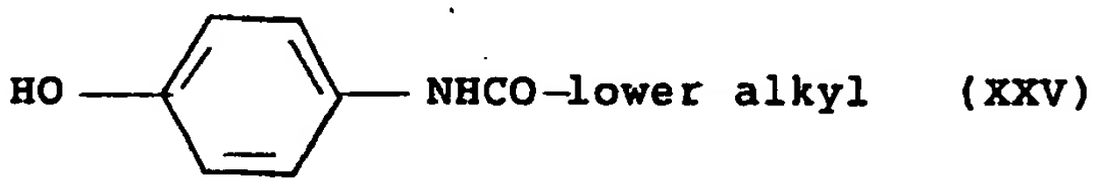
Compounds of formula (XXIII) may be prepared by nitration of compounds of formula (XXIV):



(XXIV)

where Ar is as defined in relation to formula (IC) using a nitrating agent such as concentrated nitric acid in acetic anhydride at -10° C to 0° C.

Compounds of formula (XXIV) may be prepared by reacting compounds of formula (XXV):

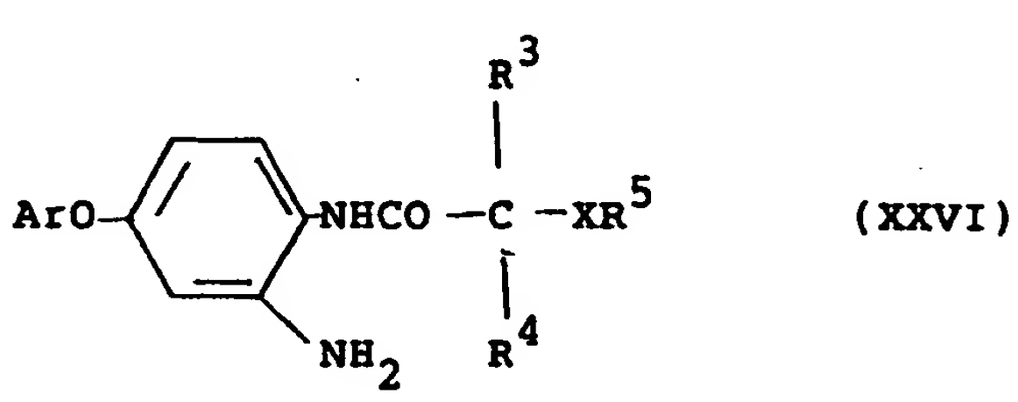


(XXV)

with compounds of formula (III) as hereinbefore defined in an organic solvent such as DMSO, DMF, lower alkylketones in the presence of a base for example alkaline metal hydroxides or carbonates at a temperature of 50-120° C.

Compounds of formula (XXV) are known compounds or may be prepared from known compounds by known methods.

An alternative method for preparing compounds of formula (IC) where W is oxygen, A is N, D is NH and B is C-$CR^3R^4XR^5$ is by cyclisation of a compound of formula (XXVI) :



(XXVI)

wherein Ar, X, R^1, R^2 and R^3 are as defined in relation to formula (IC) in the presence of a dehydrating agent such as phosphorus pentoxide at 120-160° C.

Compounds of formula (XXVI) are prepared from compounds of formula (XIX) as hereinbefore defined by reaction with a compound of formula (XXVII) :

(XXVII)